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**LA THÈSE A ÉTÉ
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AN INVESTIGATION INTO THE SOLUBILITY BEHAVIOR OF
PHOSPHORITE IN SEAWATER

by

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A THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
at Dalhousie University

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Approved by:

external examiner

"We may be able to substitute nuclear power for coal power, and plastics for wood, and yeast for meat, and friendship for isolation--but for ~~phosphorus~~ there is neither substitute nor replacement."

Isaac Asimov

(Quoted in Engineering and Mining Journal, May, 1976).

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ABSTRACT

The solubility behavior of a number of apatites in seawater was investigated. Exposure of these apatites to various solutions in which the fluoride, calcium, magnesium, total phosphate, and total CO_2 concentrations were varied created new phases at the solid-solution interface. Re-exposure to regular seawater showed that these new phases could be altered to yet other phases as a result of the change in the chemical environment. The apatite mineral surfaces and the changes that they underwent were examined using a number of surface techniques (e.g., ESCA, BET, SEM).

Exposure of apatites to sodium chloride and seawater solutions at various temperatures and pressures also demonstrated that these thermodynamic variables affect surface phase formation. The degree of mineral dissolution, monitored by solution composition change, varied inversely with temperature (pressure constant) and linearly with pressure (temperature constant). An increase in temperature or the presence of fluoride ions in solution were found to decrease pressure-induced dissolution.

The behavior of apatites in seawater can be described as an interaction with various components of seawater at the solid-solution interface which can lead to the formation of new phases on the mineral surface. The composition of these new phases is a function of the physical and chemical environment and the characteristics of the apatite. The altered surface, and not the bulk mineral phase, then controls subsequent solubility behavior and dissolution kinetics of the apatite.

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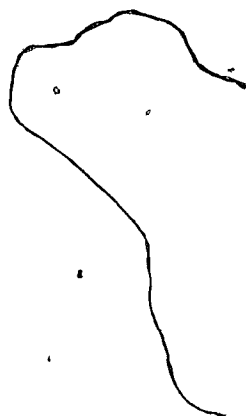
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And finally, a special thanks to my wife for her
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INTRODUCTION

I. What Is Phosphorite?

Phosphorite or marine phosphate rock is the common name for minerals high in phosphate content that belong to the apatite group of minerals. Apatites have the general formula: $M_{10}(XO_4)_6Z_2$ and are characterized by a hexagonal unit cell of the type $P6_3/m$. In phosphorite, the M sites are usually occupied by the divalent cations: Ca, Mg, Sr, or Ba; the XO_4 sites by the complex trivalent ions PO_4 and CO_3 , and the Z positions by the univalent ions: F, Cl or OH. Various solid solution combinations are possible.

Beevers and MacIntyre (1946) have suggested that apatite has a hexagonal network composed of phosphate tetrahedra, a simple anion, and a divalent cation. The structure is similar to a honeycomb, where the vertical sections are columns of "Ca-O", with the "O" supplied by the phosphate groups in the horizontal plane thus linking the columns together in a continuous fashion. The fluorine ions occur vertically above each other within channels of the honeycomb, where they are co-ordinated to additional calcium ions in "niches" within the irregular walls of the network (Figure 11).

In the natural environment, apatite does not exist as a simple pure phase but includes a large number of substituted ions. This leads to apatites of widely varying composition, even within one geological deposit (Lehr. et al.,

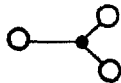
Figure I-1: Crystal Structure of Apatite Looking Down c-Axis (from Altshuler et al., 1958, based on Beever and MacIntyre, 1946)

A - Incomplete structure showing hexagonal framework and unoccupied channels

B - Addition of 3 channel calciums and a fluorine occupying same plane

C - Position of second planar group of 3 channel calciums and 1 fluorine, at a different vertical height in the structure

D - Complete structure



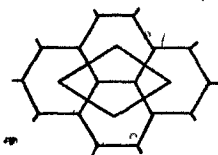
PO_4 tetrahedron,
 O_2 superimposed



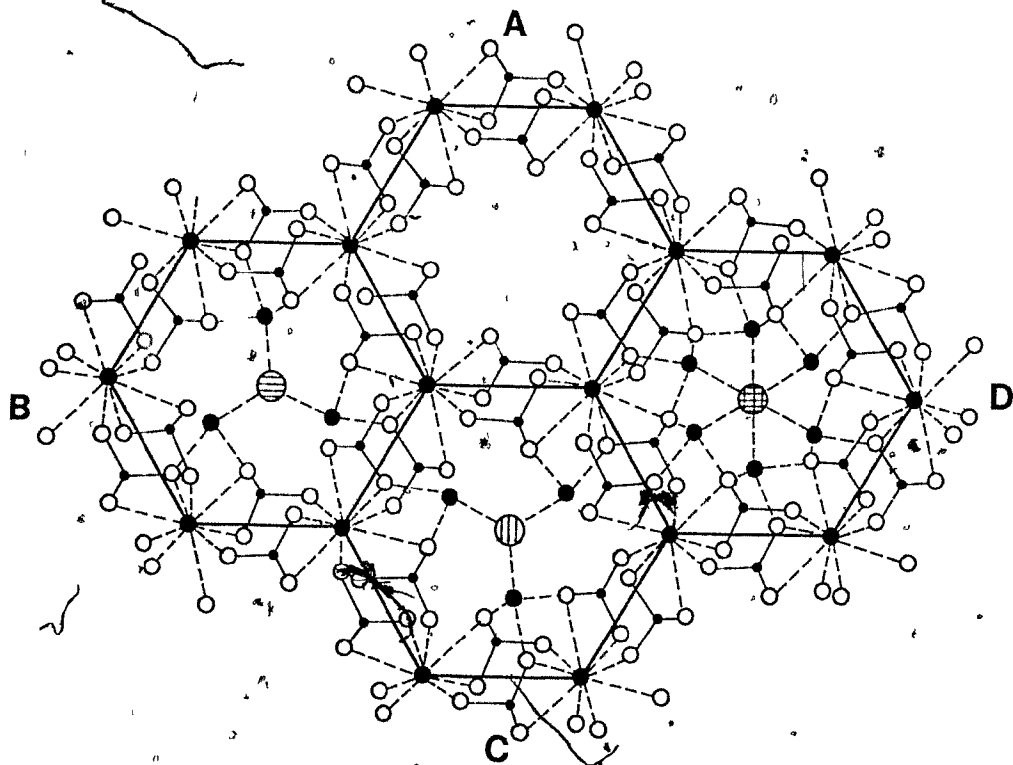
Fluorine, singly
and superimposed



Calcium



Relation of
Unit cell
to Hexagonal
Network



Whippo and Murowchick, 1967). These substituted ions are those with similarities in size and charge to the ionic components of apatite. Natural apatites often have magnesium and sodium substituting for calcium, carbonate for phosphate, and fluoride for hydroxyl. There has been considerable debate within the literature (McConnell, 1973) as to whether there "foreign ions" are truly in the crystal lattice or whether they are simply adsorbed, attached or co-existing phases. Much of the debate has centered around the carbonate substitution (McConnell, 1973). The presence of carbonate has been observed to weaken certain internal bonds within the apatite crystal thus making it more soluble than other forms of apatite. A change in the characteristic apatite morphology was also noted (LeGeros et al., 1967, a,b).

Sedimentary apatites are generally carbonate-fluorapatites (francolite) and exist as fine-grained micro-crystals often known as collophane (Whippo and Murowchick, 1967). Altschuler et al. (1958) have compared a number of analyses of sedimentary apatites and found a deficiency in P_2O_5 relative to CaO and an excess of fluoride/hydroxyl. There is generally 2-4% carbonate present. The chemical content of the marine apatites is controlled by their depositional environment and their mode of formation. Baturnin et al. (1970, 1974) have noted a wide variation in content within South African marine phosphorites.

/ II. Laboratory Studies of Apatite Solubilities

Publications from three main groups show the different approaches to the problem of apatite solubility. These publications arise from the work of: soil chemists investigating the dissolution of phosphate fertilizers in natural waters; dental scientists interested in the prevention of tooth decay; and marine geochemists studying formation of phosphorite deposits in the sea.

Very little work has been done on the problem of the solubility behavior of apatite in seawater. Recent reviews on marine apatites have been published by Bushinskii (1966), Gulbrandsen (1969) and Tooms et al. (1969).

Smirnov et al. (1958) measured the solubility product constant for a number of apatites in solutions similar to seawater and suggested that the sea was saturated with respect to hydroxyapatite. Roberson (1965, 1966) studied the solubility of some natural apatites in artificial seawater at 1 atmosphere and 25°C. He suggested that the solubility of apatite was a function of pH and reported a solubility for $\text{Ca}_5(\text{PO}_4)_3\text{F}$ as $10^{-52 \pm 1.5}$ and inferred that the bulk of the ocean was saturated with respect to fluorapatite.

Gulbrandsen (1969) comparing the results of Smirnov et al. and Roberson has suggested that the true solubility of apatite lies between the two sets of data, since Smirnov et al.'s

work was based on determinations from precipitation reactions, while that of Roberson was based on dissolution reactions.

Kramer (1964) has reported solubility product constants for a carbonate-fluorapatite of 10^{-103} (5°C) and 10^{-105} (25°C) and suggested that the oceans should be saturated or super-saturated with respect to carbonate-fluorapatite. Kramer noted, however, that ion-pairing processes, among other things, could significantly alter his calculations, and thus his conclusions.

Arrhenius (1963) suggested that phosphorites were dissolving in deep cold seawater and re-forming in warm shallow waters. He also suggested that impurities in the apatites could lead to stability in regions where apatite would be predicted to dissolve.

Gulbrandsen (1969) suggested that high phosphate concentrations in seawater would promote apatite precipitation. Other factors which promote apatite formation also might favour the formation of other minerals, the formation of which could be so extensive as to overwhelm or inhibit the apatite formation.

Atlas (1975) suggested that the solubility of apatites is dominated by solid-solution boundary reactions. The reaction of a number of apatites in 33 parts per mil seawater at 10°C, 1 atm. were studied. He suggested that a layer containing varying proportions of F^- and $HPO_4^{=}$ ions was the

most likely possibility. He did not investigate the solid surface itself, but based his hypothesis on solution concentrations and calculated that a decrease in Mg^{+2} in solution would decrease solubility, while a decrease in Ca^{+2} increased solubility. Atlas stated that apatite precipitation kinetics precludes apatite formation in open seawater, but that pore water conditions in upwelling zones allow apatite formation by direct precipitation.

Weir et al. (1971) and Chien and Black (1975) investigated phosphate rock dissolution in acidic solutions and found that the mineral had a wide range of solubilities. The most soluble fraction was dissolved rapidly, leaving a fraction that dissolved much more slowly. They suggested that this multi-stage process might be due to poor crystallinity found in sedimentary apatites. Chien and Black (1976) also found that an increase in the carbonate content of the apatites causes an increase in solubility, but only when the alkaline-earth carbonates had been first extracted. The presence of these "impurity" carbonates could alter the apparent solubility product significantly. They found that there was a linear variation in the free energy of formation of the mineral with carbonate content. Depending on the extraction technique used, values of $\Delta G = -3094.5 + 124.9 \times$ (mole frac. carbonate) to $= 3104.4 + 130.2 \times$ (mole frac. carbonate) (kcal./mole⁻¹) were reported.

7

Duff (1971a,b) found in his investigations of apatite-water systems that a decrease in $H_2PO_4^-$ activity or an increase in fluoride activity extended the stability field of apatite into the acidic pH region (i.e., made apatite less soluble). In general, apatite is the most likely calcium phosphate in the pH = 8 region. Increased hydroxyl content in fluorapatite alters its stability field by increasing its solubility. This effect is most pronounced when the hydroxyapatite-fluorapatite is more than 80% hydroxyapatite.

Simpson (1966, 1967, 1969), in his investigations of apatite precipitates, found that varying the ionic concentrations in the solution by small amounts could alter the composition of the precipitated phase. Low magnesium content in solution caused the formation of non-apatite calcium phosphates, but the introduction of small amounts of fluoride or chloride overcame the magnesium effect and aided the formation of apatite. Apatite strongly adsorbs fluoride, but Simpson found that concentrations of fluoride 10^2 to 10^3 times that found in seawater were necessary to permit the formation of fluorapatite. The high concentration of fluoride required indicates that fluorapatite formation is most likely to occur in pore waters. However, the ability of apatite to adsorb fluoride strongly and the low solubility of fluorapatite compared to the other forms of apatite, indicates that the blocking of active surface sites, perhaps through the mecha-

nism of a phase on the solid surface, occurs fairly rapidly and that this process "protects" the remainder of the apatite from dissolution. Complete fluoridation is probably achieved by subsequent solid diffusion.

Martens and Harriss (1970) have suggested that the presence of magnesium in seawater prevents the formation of apatite. They found that apatite-like precipitates were only formed in solutions where the calcium to magnesium ratio exceeded 5. Bachra et al. (1965) found that magnesium stabilized the formation of amorphous calcium phosphate, disturbing the crystallinity of apatite. Simpson (1966a) has noted, however, that low fluoride or chloride concentrations can eliminate this magnesium effect.

Although the literature on dental investigations of hydroxyapatite dissolution and the effect of fluoride ions is very extensive, only more relevant papers will be discussed here.

Higuchi and co-workers, (Higuchi et al., 1965; Higuchi et al., 1969; Mir and Higuchi, 1969; Nelson and Higuchi, 1970; and Dedhiya et al., 1973, 1974) on the basis of solution concentration measurements and computer modelling, have suggested that when hydroxyapatite is exposed to salt solutions a new mineral phase on the apatite surface forms, the composition of which is a function of the solution composition. They suggest that fluorapatite is more likely formed

by the exchange of fluoride for hydroxyl species in the apatite rather than by precipitation of a complete fluorapatite. Young et al. (1969) have found that only small concentrations of fluoride within the hydroxyapatite structure can significantly reduce the solubility of hydroxyapatite. They suggested that this decrease in solubility is due to the increased hydrogen bonding to the fluoride ions, which effectively "traps" the hydroxyl ions and prevents their diffusion, thus preventing the dissolution of the apatite. Higuchi and co-workers also noted that combinations of various ions in solution decreased the solubility more than was predicted by the behavior of either of the species acting singly. This synergistic effect is probably the result of a strengthening of the crystal bonds by the creation of a less-soluble (than hydroxyapatite) apatite. Alteration in ion-pairing due to ionic activity changes in solution could also contribute to the synergistic effect.

McCann (1968) found that the presence of trace impurities in apatite enhanced the solubility more than was predicted by theory. This effect was especially noticeable in solutions of high pH where apatite solubility was normally lowest. Higher solubilities of apatite than predicted by theory in high pH solutions could also be due to increased fluoride-hydroxyl exchanges caused by the increase in hydroxyl ion activity. The pH at which sufficient calcium and fluoride

was dissolved from the apatite to equal the solubility product of CaF_2 was increased by the presence of small quantities of fluoride and decreased by the addition of Ca or P. With sufficient solid, however, equilibration with both solids (CaF_2 and fluorapatite) was likely. Farr and Elmore (1962) have noted that supersaturated solutions can remain stable for both CaF_2 and fluorapatite for long periods of time without precipitation, so that the apparent solubility product can be exceeded without there being precipitation. Nucleation material or an active surface are very necessary for active precipitation and for the prevention of supersaturation.

Hagen (1975) found that the solubility product for fluorapatite was unaffected by particle size or solid/solution ratio. His result may have been due to incongruent dissolution processes, since the Ca/F, P/F, and Ca/P ratios were all higher in solution than in the solid.

III. Surface Studies

A number of investigators have suggested that a surface phase is formed when apatites are exposed to solution and that this new mineral phase then controls subsequent solution-solid interactions:

Arnold (1950) was one of the first to suggest that a surface complex formed on hydroxyapatite. He suggested that

hydroxyl groups adsorbed and were incorporated where columns of calcium ions within the crystal structure were exposed at the surface. This would give a calcium-rich surface layer, $\text{Ca}_{12}(\text{PO}_4)_6\text{OH}$. On the other hand; Rootare et al. (1962), have suggested a phosphate-deficient surface caused by the hydrolysis of terminal phosphate ions, giving an intermediate complex, $\text{Ca}_2(\text{HPO}_4)(\text{OH})_2$. Deitz et al. (1964) have admitted that there is no crystal species of this formula and it is only likely to be an intermediate. Dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) does exist as a separate chemical crystal and its presence has been noted on the surfaces of exposed hydroxyapatite (Francis, 1965). Dietz et al. (1964) noted that the solubility product for hydroxyapatite varied significantly with variation in solid/solution ratio. The theoretical $\text{Ca/P} = 1.67$ for hydroxyapatite was only attained in solution after an appreciable fraction of the material was dissolved.

Smith et al. (1974) have also found that varying the solid/solution ratio caused a variation from the predicted molar ratio of Ca:P of 1.67 in solution when the solid/solution ratio was high. This was especially true when the ratio exceeded 3g/100 cc.

Arnold (1950) and Rootare and co-workers (Rootare et al., 1962, Deitz et al., 1964) both suggest that the dissolution process is most unlikely to take place on the a-b crystal

face, whereas Kukura et al. (1972) suggest that the a-c face is the more likely dissolution site. Smith et al. (1974) suggest that both the a-b and the a-c faces are suitable for dissolution and probably all faces should be considered in the dissolution process. The question of which face is the most likely site for dissolution could be part of the multi-stage dissolution process. The ability of a crystal face to withstand dissolution processes may be related to the strength of the chemical bonds within the crystal and the degree of crystallinity on a crystal face. Both of these mechanisms have been suggested to be the cause of the multi-stage dissolution of heterogeneous solids.

The involvement of different crystal faces in the dissolution process may also be caused by the presence of certain ions in solution. Bell et al. (1973) found that when there was low F^- in solution, F^- replaced OH groups in channels parallel to the c-axis of the apatite crystal, whereas at high concentrations of F^- , replacement of OH groups attached to surface calcium ions also takes place.

A few studies of the actual mechanisms of apatite-solution interactions, based on zeta potential measurements, have been made. Somasundaran and Agar (1972) suggested that phosphate, hydrogen, and hydroxyl ions are all potential-determining ions. The influence of calcium is due to specif-

ic adsorption on the surface. Fluoride interactions are very complicated due to complex chemical reactions and reconstruction of the original surface phase. This was similar to the findings of Saleeb and De Bruyn (1976).

Somasundaran and Agar (1972) suggest that at high fluoride concentrations, CaF_2 formation is likely and the precipitation of this compound, as well as the formation of fluorapatite, may cause the anomalous behavior of fluoride and its effect on the zeta potential.

Atlas (1975) suggested that a surface phase for apatites is dependent mainly on F^- and HPO_4^{2-} ions. He found that the variation in HPO_4^{2-} in solution was linear with the variation in surface area (solid/solution ratio), whereas the variation in PO_4^{3-} was definitely non-linear. He also suggested that surface phase formation would lead to an apparent multi-stage dissolution process, where the apparent equilibrium is in reality a steady-state process with competing kinetic processes involving various surface phases, as well as the original bulk phase, in the dissolution process. Roberson (1965, 1966) has also suggested that a more soluble surface layer existed initially on his apatites.

Terjesen et al. (1961) have suggested that "foreign" ions inhibit dissolution of low-solubility carbonates by promoting the rate of reverse reactions. This theory is completely different from the crystallization-dissolution

theories of Burton, Cabrera and Frank, 1951; Burton and Cabrera, 1949; Cabrera and Burton, 1949; Frank, 1949), recently reviewed by Davey (1976). They suggest that the dissolution process occurs at steps and kinks along a crystal face and that the inhibition of the dissolution process occurs when "foreign" ions occupy sites at the steps and kinks. This restricts the dissolution process by altering the surface free energy. Davey (1976) suggested that impurities which are structurally similar to the crystal components of apatite (for example, F^- , $r = 1.36\text{\AA}$, OH^- , $r = 1.40\text{\AA}$) may be the most effective in the inhibitory processes at the kink and step sites. Other, bulkier "foreign" ions (for example, organic molecules) cause inhibition at ledge sites and are thus less effective in inhibiting dissolution.

IV. Objectives of this study

Extrapolation from data obtained by allowing simple solutions to react with pure apatite crystals, like hydroxyapatite, to the behavior of apatites in the marine environment with its complex solutions and even more complex assemblage of solids in the sediments is very difficult. Although phosphorite and phosphate species are relatively rare in the oceans, they are important building blocks in the biological cycle. Loss of phosphate to the

sediments and its subsequent mineralization can be a significant part of the phosphate cycle in the oceans. This study is an investigation into the chemical and physical processes that promote or inhibit the dissolution of phosphorites in the marine environment.

A number of questions were proposed as objectives of this investigation:

- (1) How rapidly does apatite achieve a stable rate of dissolution when exposed to seawater?
- (2) What are the effects of solution activity changes (due to chemical reactions within the confines of interstitial water chemistry) on apatite dissolution from the point of view of (a) the solution (b) the solid?
- (3) What are the effects of temperature and pressure on dissolution?
- (4) What kind of alteration of the mineral surface occurs when it is exposed to solution and how extensive is this alteration?
- (5) How can the physical and chemical environment be related to the form, extent, and composition of the altered mineral surface?
- (6) What time scale is involved in the surface alteration and what are the effects of the alteration on the time scale of dissolution?

Environmental effects are very important in investigations of marine geochemical cycles. Theory may predict the dissolution of a mineral which in reality undergoes no dissolution. The alteration of the original surface may be the "missing link" in this debate. Alteration of the surface of apatite may be related to the strong ability of apatite to concentrate uranium and trace metals from seawater.

EXPERIMENTAL

I. Materials

Reagents used were supplied by Fisher Scientific, except for the NaF (BDH Co.) and the LaCl_3 (Anachemia).

Calcium and magnesium standards were prepared as dilutions from stock 1000 ppm solutions (Fisher).

The land apatite samples were purchased from Ward's Scientific. The marine sample was a generous gift from Dr. A. Soutar of the Scripps Institute of Oceanography. The sample was part of a dredge haul from the Peruvian upwelling zone, $19^{\circ}30'S$ $70^{\circ}20'W$, 128-132 m of water. The rock samples were crushed by a mechanical jaw crusher and sieved to the desired size. The samples were carefully washed with de-ionized water before exposure to the solutions.

The seawater was piped into the laboratory from a section of Halifax harbour and passed through a series of filters. The chemical characteristics were: salinity: 3.1%, Ca: $9 \times 10^{-3}M$, F: $2 \times 10^{-5}M$, tot. phosphate: $2 \times 10^{-6}M$, and pH about 7.9.

II. Apparatus

A. Pressure System

In order to simulate more closely the type of environmental conditions which could affect phosphorite solubility, a system in which seawater could react with phosphorite while

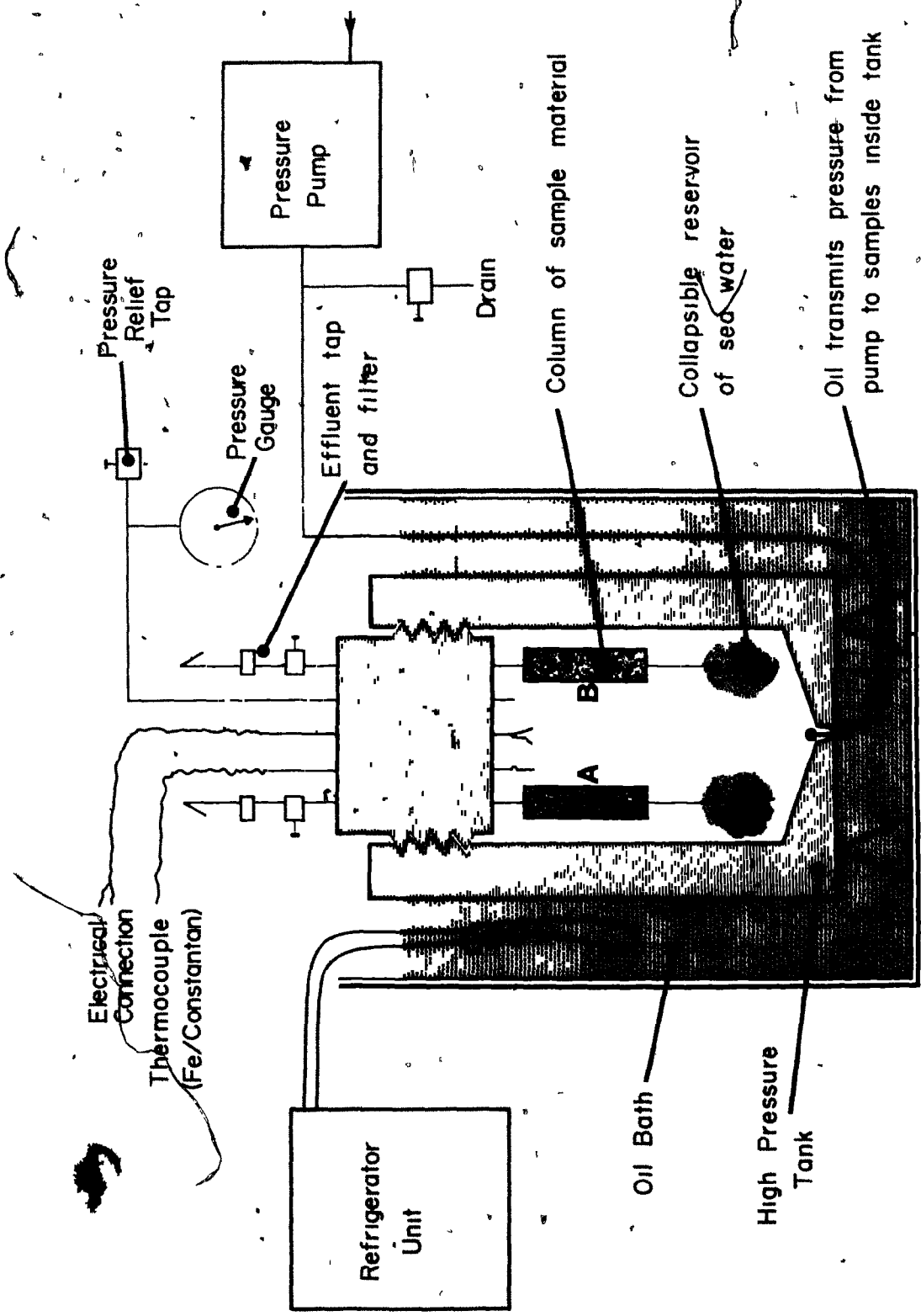
the total system was under pressure was constructed (Figure E1).

A pressurized steel cylinder was immersed in a constant temperature bath (5-6°C). Temperature was monitored by means of an iron/constantan thermocouple inside the cylinder. Pressure was transmitted by oil (Votesso 35, Imperial Oil Ltd.) from an air-driven pump. Pressure was monitored by an external Heise gauge, 0-1200 \pm 1 Atm. The stainless steel fittings, cylinder, gauge and pump were purchased from High Pressure Eqp., Erie Pennsylvania, U.S.A.; fittings for the systems inside the cylinder were either stainless steel Swagelock compression fittings or Chromatronix (Spectra-Physics) plastic/teflon fittings.

The reaction system consisted of a collapsible Cubitainer, purchased from Cole-Parmer Ltd., as a solution reservoir, connected to a column of material by a length of 1/16 in. O.D. Teflon spaghetti tubing. The column was constructed from polyethylene tubing, 18 cm x 1 cm I.D., plugged at each end by glass wool and a rubber stopper. The column was connected to a high pressure control valve on the outside of the pressure cylinder by a length of 1/8 in. O.D. stainless steel tubing (thick wall). In normal operation two identical systems were used simultaneously.

As effluent was removed through the control valve, the pressure within the cylinder forced liquid from the reservoir

Figure E1: High Pressure Apparatus

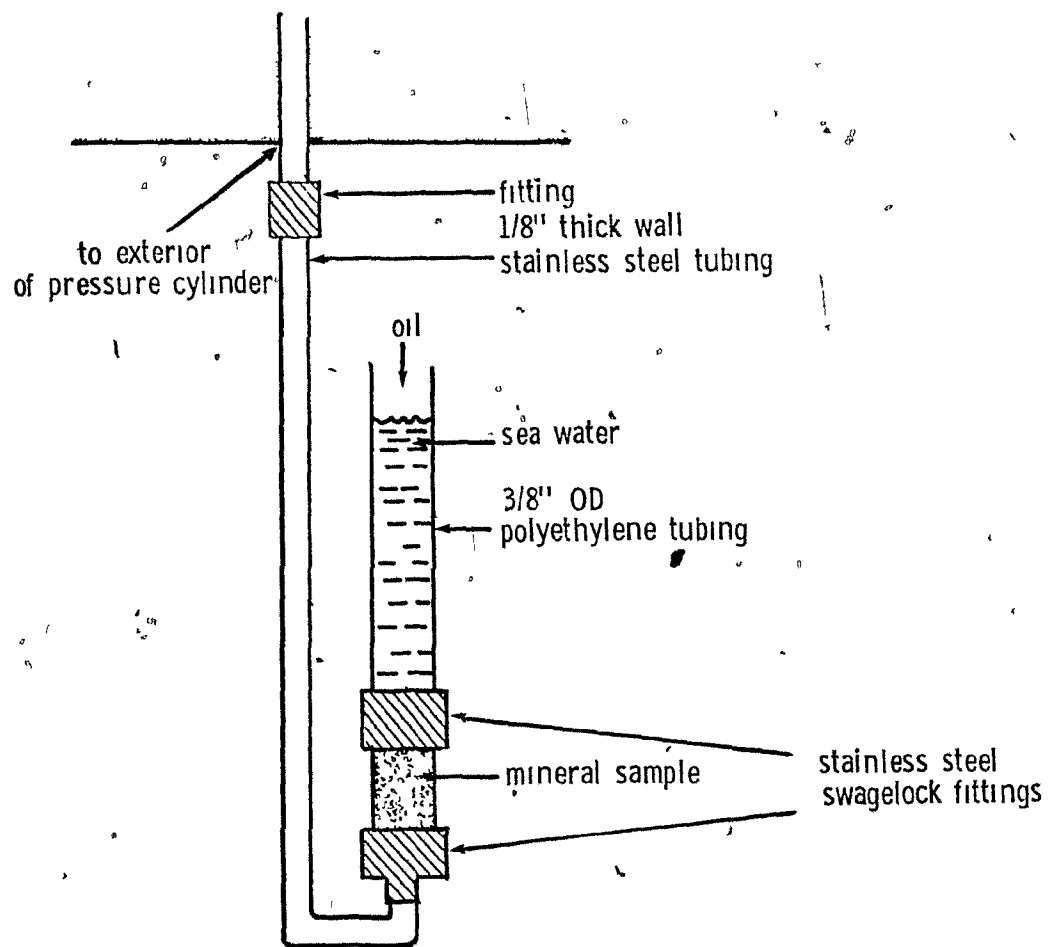


up into the column. The first 1 cc of effluent was discarded as this represented liquid sitting in tubing between the control valve and the top of the sediment column. Effluent was removed as two 10 cc samples, at a flow rate of less than 1 cc/min. With the size of material and the flow rate used, no in-line filtration was found necessary.

During solution sample withdrawal, the pressure and temperature were maintained constant. Control experiments with empty columns indicated that there was no contamination from the system plumbing.

In order to examine the solid surface that had been exposed to seawater at various high pressures, a new system (Figure E2) was devised. In this system short lengths of polyethylene tubing were used, one as a water reservoir and the other as a sample holder. As water was pressed through the high pressure valve on the pressure cylinder, oil could flow into the water reservoir through the open end of the tube. As more water was expressed, oil entered the sample holder and coated the mineral samples. During this replacement of water by oil, the pressure of the system was maintained constant at the desired level. Once oil had covered all the mineral surfaces and there was no more water present, the pressure was decreased to 1 atmosphere. In this way the surface that was exposed to seawater at an elevated pressure was preserved for later examination. Experiments were con-

Figure E2: High Pressure System Used for Study of
Solid Surfaces



ducted which showed that once the surface was coated with oil no further solution-apatite reactions occurred at any pressure.

B. Suspended System

The rock samples and the solutions were allowed to come to temperature equilibrium before mixing. The suspensions were generally 5 or 10g/100 cc of 8-28 mesh apatite. The suspensions were shaken in 125 cc polyethylene bottles on a Burrell wrist-action shaker. The 2°C experiments were carried out in a special constant-temperature room, the 25° experiments in the open laboratory, and the 50° tests in a Wilkens-Anderson Lo-Temp constant-temperature bath.

A separate suspension was used for each time interval. This gave a 100 cc sample, which after filtration (Millipore 47 mm x 0.45 μ) was split into two 50 cc samples for duplicate analysis. For the experiments with alkalinity variation, 1000 cc bottles containing 50 g of material were used. 50 cc samples of solution were removed by syringe: 20 cc was used for regular analyses and 30 cc was used in measuring total CO₂.

III. Analyses

A. Solution

The effluent from the pressure experiments was collected

as two 10 cc samples. The pH for each sample was measured immediately using an Orion 801 pH meter and a Fisher pH electrode. The hydroxyl ion concentration was calculated from this pH and the appropriate K_w (Weast et al., 1967). The effluent was examined closely and samples containing solids or oily films were discarded. Samples from the suspension system were handled similarly.

Calcium and magnesium were analyzed using a Perkin-Elmer 403 atomic absorption spectrometer with an acetylene-air flame. The analysis procedures are outlined in the manufacturer's handbook (Perkin-Elmer, 1968). Samples were diluted with de-ionized water, so that the concentrations fell within the linear response range of the instrument (0.1-7 ppm Ca; 0.05-0.7 ppm Mg). The diluted samples contained 0.5-1% La to eliminate phosphate interferences.

The fluoride concentrations were measured with an Orion fluoride specific-ion electrode and an Orion 801 meter. The analysis was based on the method of Warner (1971).

Inorganic phosphate was measured spectrophotometrically on a Cary 14 (Varian) spectrophotometer at 885 nm, using the method outlined in Parsons and Strickland (1972).

Total carbon dioxide was measured only for the alkalinity variation experiments. The procedure (Cooke, 1976) involved injection of 5 cc of sample into a flask of concentrated phosphoric acid. The low pH forced all the carbonates

to CO₂ which was then sparged from the flask by a stream of dry, clean N₂. The gases flowed into a Beckman 315L infrared analyzer. The CO₂ content was monitored as a voltage response on a Hewlett-Packard 34750A digital voltmeter and 5150A thermal printer. Calibrations were based on stock solutions of 2K₂CO₃·3H₂O.

In each analysis, standards were prepared and run at the same time as the samples, so that instrument variations could be neglected.

B. Solids

X-ray diffraction patterns were obtained using a North American Phillips goniometer with a copper K α source and a nickel filter. Most of the scanning electron microscope work was done using a Cambridge Stereoscan 600 SEM. Energy dispersion analyses were done by the staff of the DREA Dockyard Laboratory, using an AMR 1000 SEM.

ESCA (Electron Spectrometer for Chemical Analysis) analyses were carried out on unreacted samples and samples that were exposed to seawater spiked with 500 ppm NaF, at the Department of Chemistry, University of Western Ontario (MacPherson ESCA-36). Analyses on samples exposed to regular seawater and seawater spiked with 500 ppm NaF at various pressures were performed at AEI Scientific Apparatus Ltd.,

Manchester, U. K. Some of the samples sent to Western Ontario were argon ion-etched, but the depth of etching was not measured.

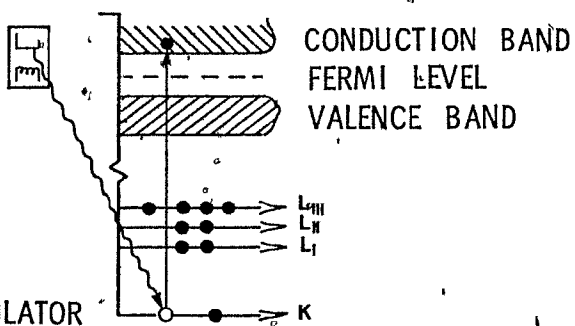
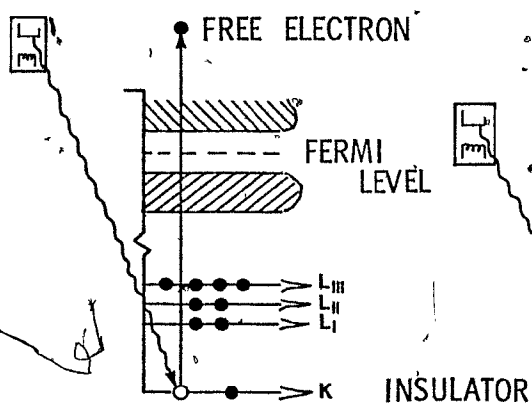
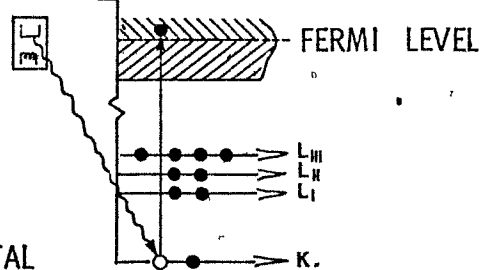
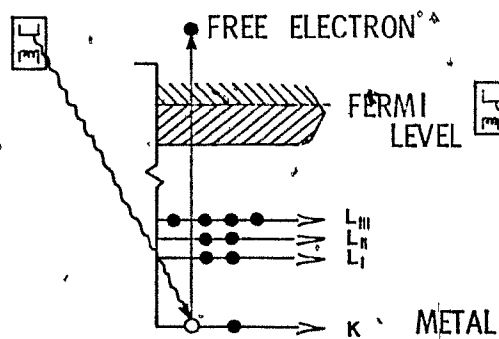
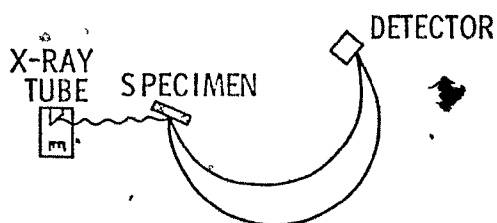
Because of the relative newness of the ESCA technique in geochemistry, a brief explanation will be given here. A more detailed discussion can be found in Siegbahn et al. (1967), Delgass et al. (1970) and Sevier (1972). In ESCA, more correctly called X-ray Photoelectron Spectroscopy, the sample is irradiated with an x-ray beam of known energy and ejected photoelectrons from the sample are analyzed in a magnetic or electrostatic detector. In X-ray absorption spectroscopy, the sample is also irradiated with x-rays, but the absorption of the x-ray beam is measured as a function of the x-ray energy. A comparative diagram of the two processes is given in Figure E3. (Siegbahn et al., 1967).

In the ESCA process, the total energy, $h\nu$, of the impinging x-ray beam is absorbed by a surface and part of the energy, equivalent to the binding energy of an electron, E_{bind} , is used to bring the electron from an original energy level to the Fermi level, thereby "freeing" the electron. As the ejected electron leaves the surface of the sample, a certain amount of kinetic energy is lost; this is called the work function of the sample. As the sample enters the spectrometer it gains some kinetic energy, and this is called the work function of the spectrometer. Thus the final de-

Figure E3: Comparison of X-ray Photoelectron and
Absorption of Spectroscopy processes
(Siegbahn et al., 1967)

ESCA

X-RAY ABSORPTION



tected kinetic energy is:

$$E_{kin} = h\nu - E_{bind} - \phi_{spec} - \Delta E_{char}$$

The term ΔE_{char} (always positive) is an additional correction term to allow for the change in behavior during analysis of insulator-type materials.

An example of the graphical output is given in Figure R 10. In this case the binding energy was recorded over the 0-1000 eV range which corresponds to a kinetic energy range of 1250 to 250 eV.

A number of peaks are denoted as "Auger". These are produced by a type of radiation less electron transition and they can also be used for surface analysis. In the Auger process, an excitation process can cause the ejection of an inner-shell electron. The de-excitation process involves the filling of this inner-shell "hole" by an outer shell electron. The energy released during this process, rather than being released as x-ray fluorescence, causes the ejection of another outer-shell electron, the so-called Auger effect. This radiationless de-excitation process occurs most likely for elements of atomic number less than thirty. For elements higher in atomic number, x-ray fluorescence is the more probable de-excitation mechanism.

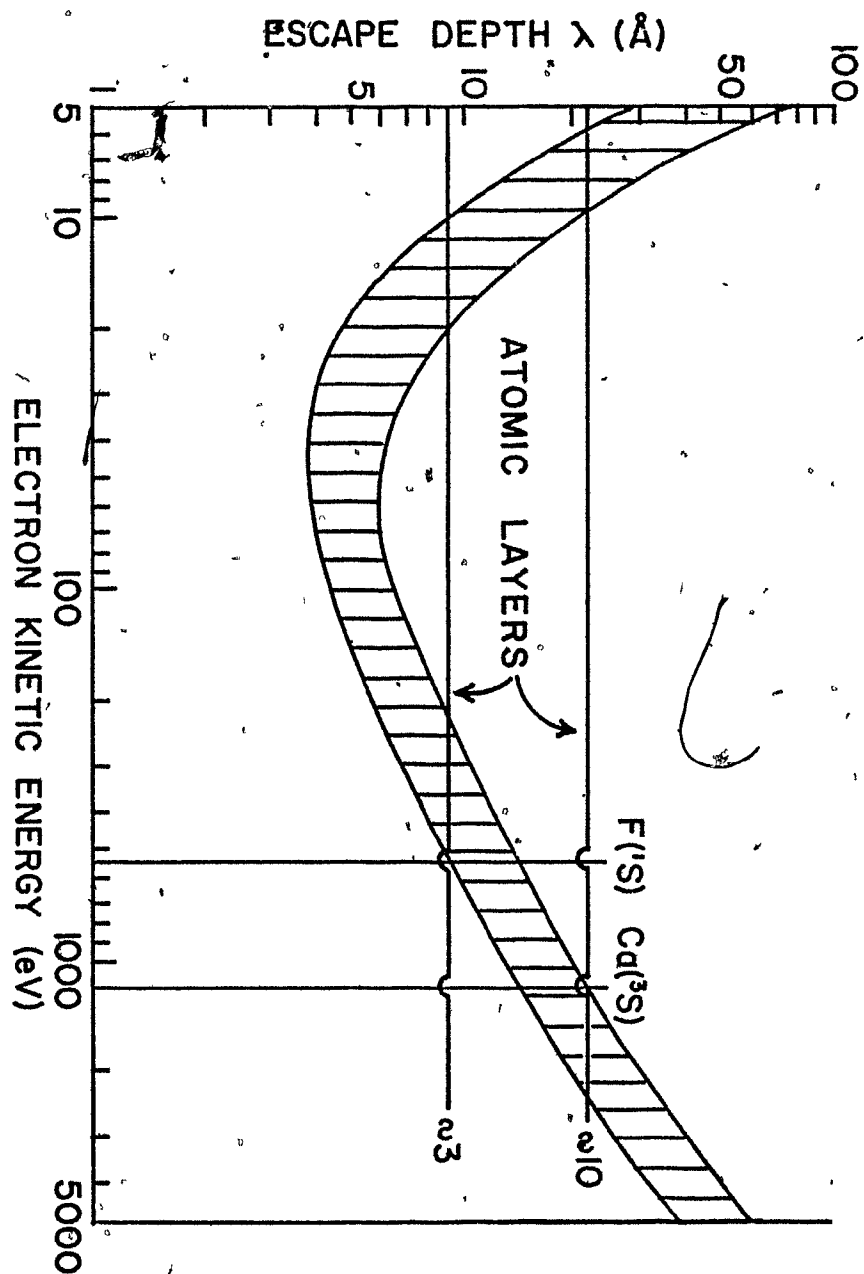
The usefulness of ESCA in surface analysis is due to the fact that only electrons ejected from the top fifty

Angstroms or less of depth are actually detected, although the initial x-ray beam may penetrate much deeper (Figure E4). Since each electron within a solid has a discrete binding energy, depending on the element, the spectrum plot gives an indication of the elemental composition of the solid. By measuring changes from the predicted position of peaks on the binding energy scale, a measure of the "chemical shift" due to chemical bonding can also be obtained.

Bulk chemical analyses were carried out in the geochemical laboratories of the Department of Geology under the direction of Dr. Muecke. Fluoride analyses were carried out by the investigator using the specific-ion electrode method of Duff and Stuart (1970). A complete physical and chemical description of the samples can be found in Appendix A.

Figure E4: ~ Escape depth of excited electrons when a surface is exposed to X-ray Photoelectron Spectroscopy





RESULTS°

I. Solid

A. Reaction with Seawater at 1 Atmosphere

A.I. Reaction with Unspiked Seawater

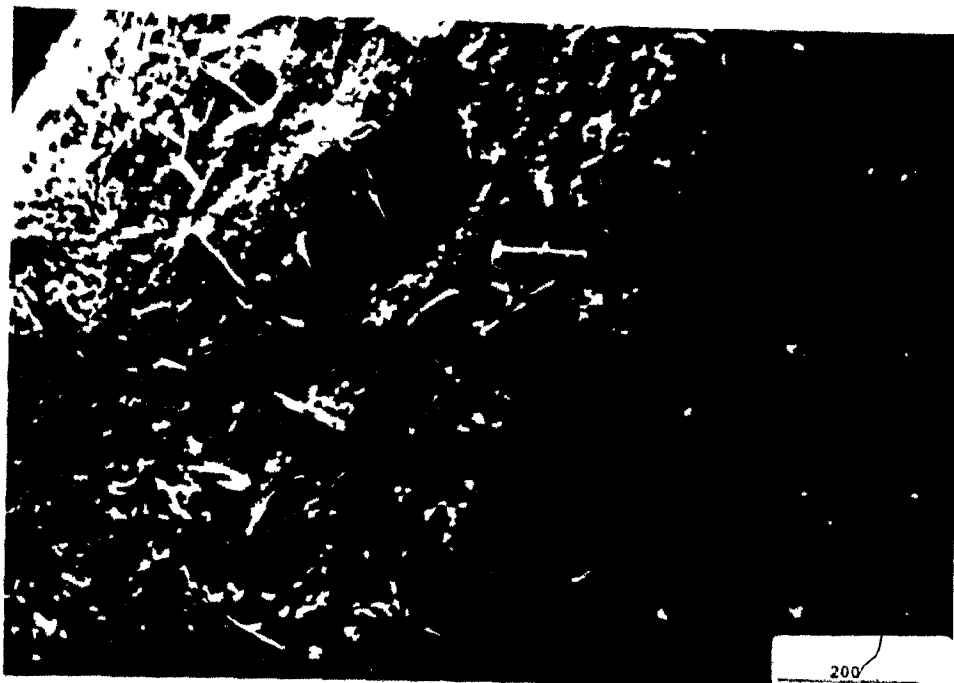
The various unreacted apatites have been characterized physically and chemically in Appendix A.

The electron micrographs of the marine phosphorite show an extremely coarse surface (Figure A3II), with some evidence of the remains of marine tests (Figure A3III). After exposure to seawater (2°C, 1 atm., 8 days), electron micrographs of the surface (Figure R 1) show the formation of a large number of hexagonal crystals, with some of the crystals grouped in "rosettes". These crystals are similar to the typical apatite structure described in Deer, Howie, and Zussman (1966). Burnett (1974) has shown electron micrographs of apatite crystals from freshly dredged marine apatite, but his crystals were only visible at magnifications greater than $\times 10,000$.

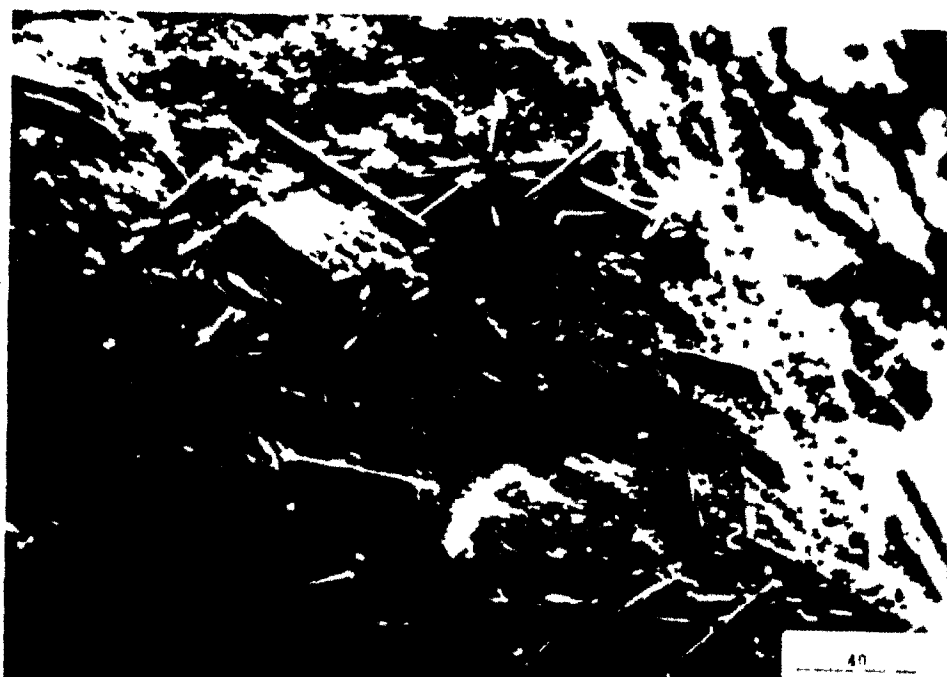
Electron micrographs of Ontario apatite (Figure A3IV0 unexposed, show a "velvety" surface covered with small shunks, which are probably the result of the preparation process. After exposure to seawater, the surface was covered in small square crystals (Figure R 2). These crystals are probably better crystallized material left behind when seawater dissolved disorganized, more soluble surface material.



Figure R1: Marine Phosphorite Reacted with Seawater
(1 atm., 2°C, 8 days)



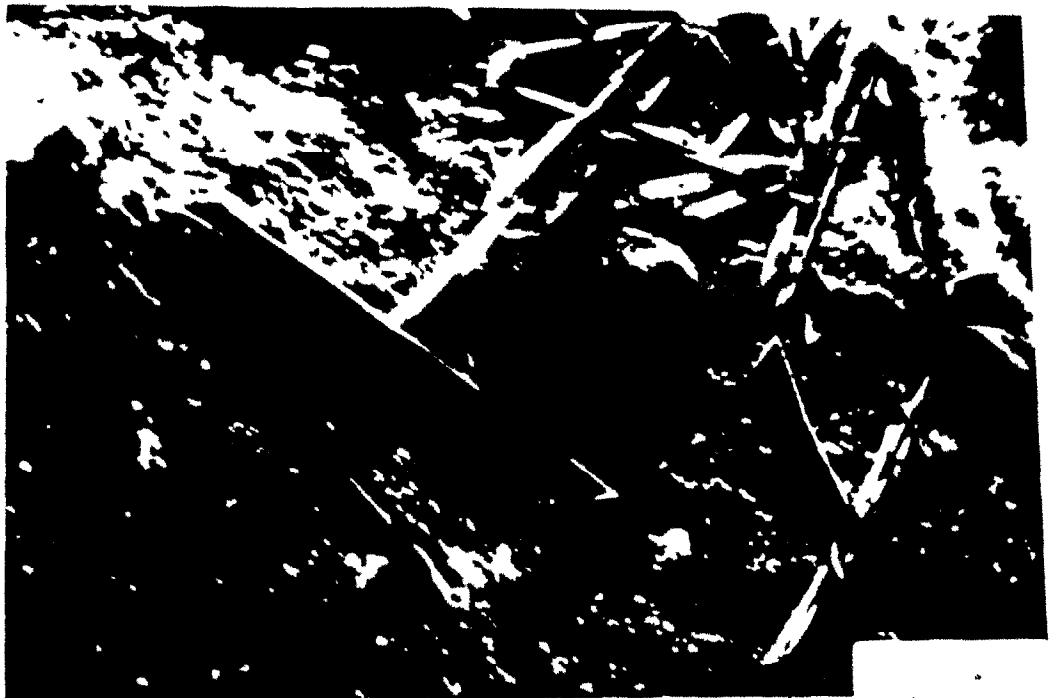
a



b



2



3

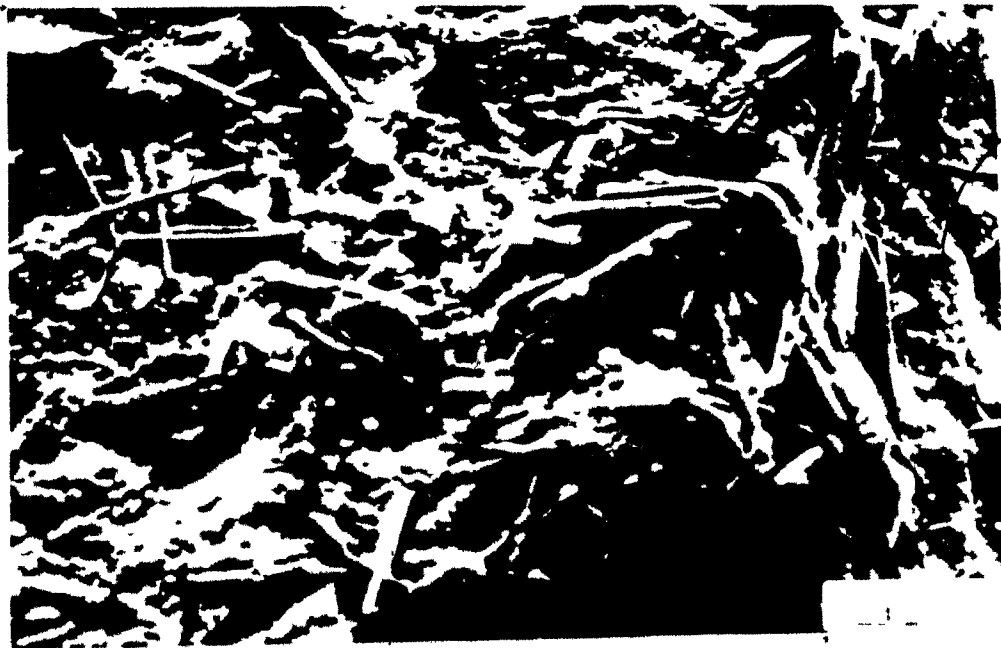
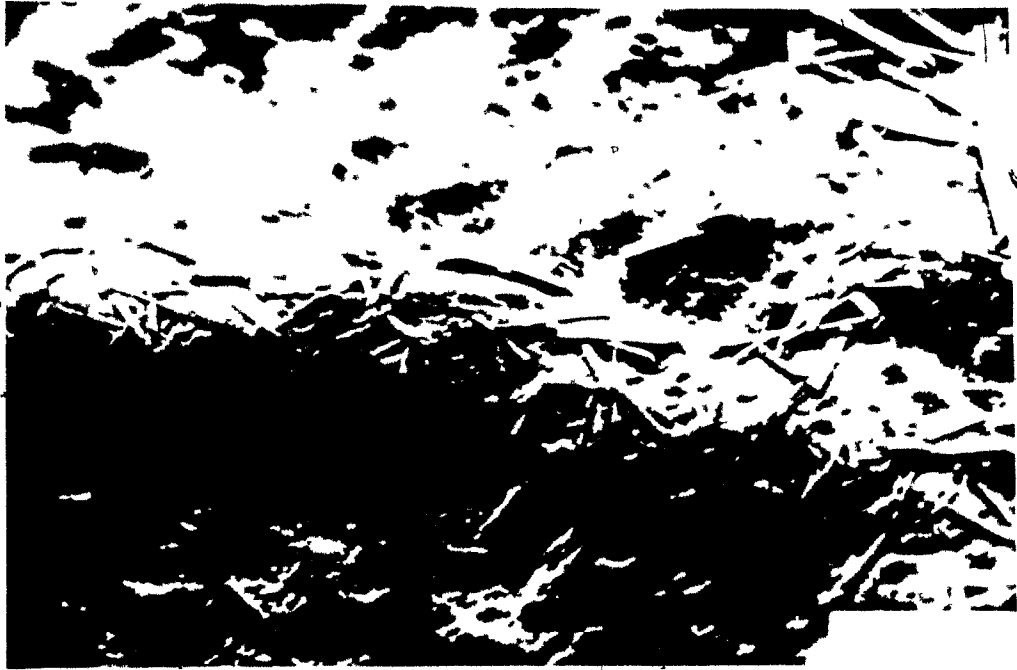
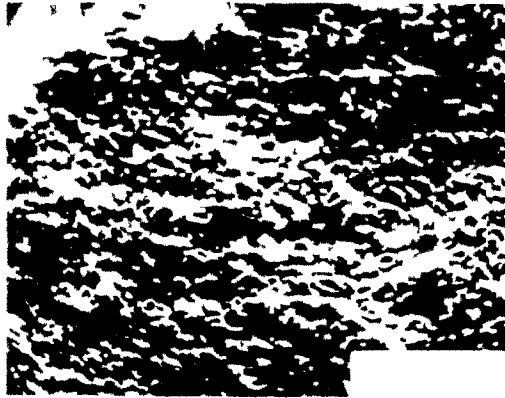
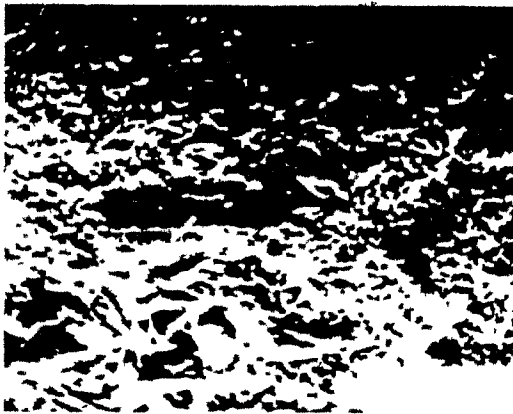
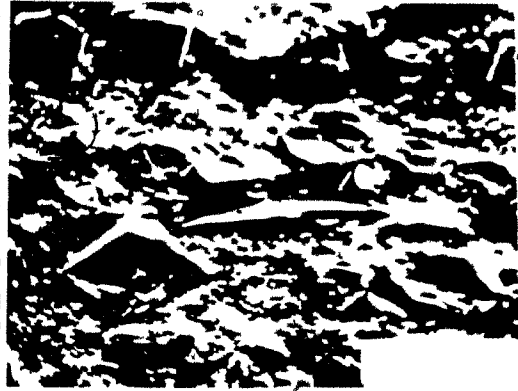


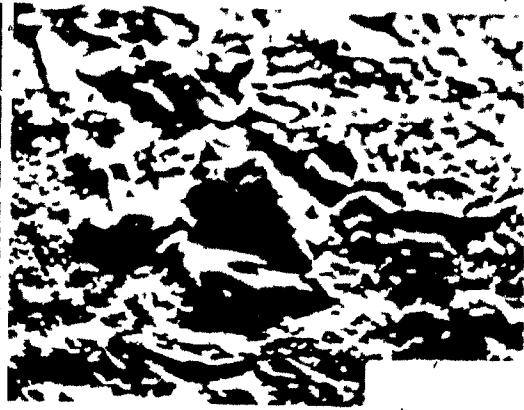
Figure R2: Ontario Apatite Reacted with Seawater
(1 atm., 2°C, 8 days)



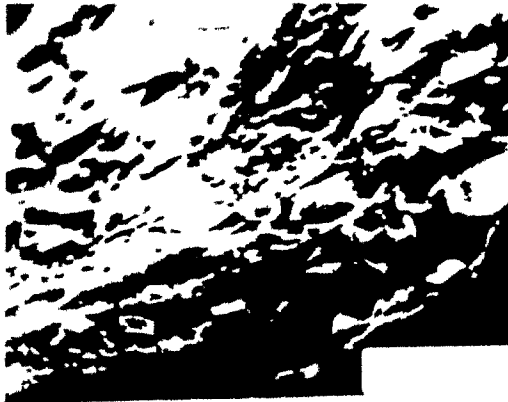
a



c



d



e



Quebec apatite had a similar "velvety" appearance before reaction with seawater (Figure A3I d,c); but after exposure to seawater the only obvious morphological change was the "weathered" appearance of the surface (Figure R 3).

Before exposure to seawater, electron micrographs of the Mexican apatite (Figure A3I, a,b) showed distinct hexagonal crystals aligned in one direction. Various dislocated chunks and needles were considered to be due to crushing processes during sample preparation. The Mexican samples were observed to have a series of alternating light and dark bands (Figure A1), but no morphological feature in the electron micrographs could be found to correspond to these stripes. A "weathering" effect was noted (Figure R4a) over most of the exposed surface, with the hexagonal crystals rounded off and smoothed out. This is similar to the crystal dissolution process described by Burton et al. (1951), Frank (1949), and Burton and Cabrera (1949).

On a few locations rod-like crystals were noted (Figure R 4). These crystals were at first believed to be rolled sheet silicates, such as halloysite (Bates et al., 1955). Further investigation indicated that they were more likely to be apatite containing a small percentage of carbonate. LeGeros et al. (1967 a,b) found that increasing the content of carbonate changes the crystal morphology from needle-like

Figure R3: Quebec Apatite, Reacted with Seawater
(1 atm., 2°C, 8 days)

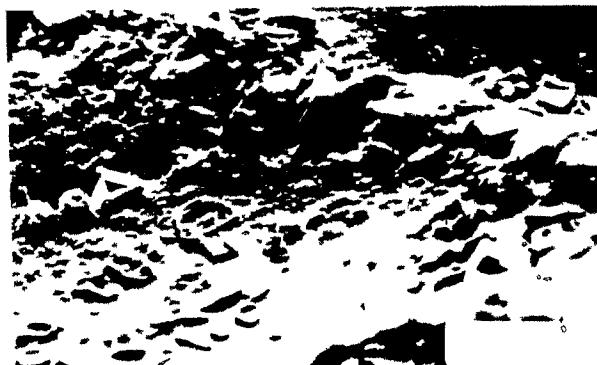
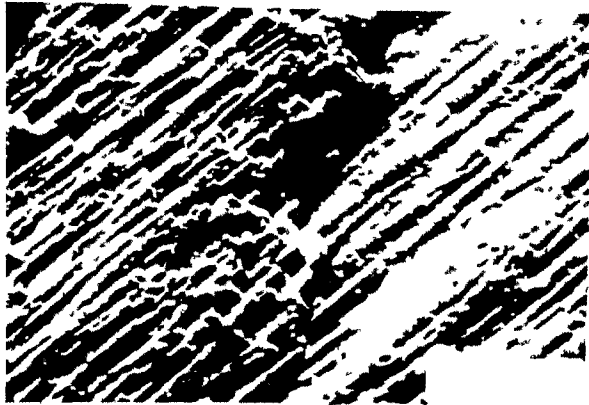


Figure R4: Mexican Apatite Reacted with Seawater
(1 atm., 2°C, 8 days).

In #c the small chunks to the right of the tube are hexagonally shaped and believed to be apatite.



a



b



crystals to rod-like structures or to more circular-shaped crystals when the carbonate percentage content varied from 0.5% to 18% (by weight).

A.II. Reaction with Phosphate-Spiked Seawater

Electron micrographs of Mexican apatite, which had been exposed to seawater spiked to give a concentration of 50 micromolar phosphate (1 atm., 2°C, 8 days) (Figure R 5), showed the formation of a number of plate-like structures which could be a type of calcium phosphate. Unfortunately, no electron micrographs of the various calcium phosphates have been published, so that exact identification was not possible through morphological comparison.

A.III. Reaction with Seawater of Altered Ca/Mg Ratios

Ontario apatite samples were reacted with seawater, which had been mixed with artificial seawater (Kester et al., 1967) to give various Ca/Mg ratios (2°C, 1 atm., 8 days). Electron micrographs of the five exposed surfaces showed the presence of square-shaped crystals which appeared to have steps into their centres. Electron dispersion analysis of the crystals gave essentially the same composition as the remainder of the surface. As for the samples exposed to regular seawater, the crystals seen are probably the result

Figure R5: Mexican Apatite Exposed to Seawater +
50 micromolar Phosphate (1 atm., 2°C, 8 days)



a



b



c



d

of dissolution of disorganized, more soluble surface material. Rowles (1968) has suggested that high magnesium content in the supernatant liquid would tend to cause the precipitation of magnesium-calcium phosphate. But, as for the Mexican apatite, no electron micrographs are available for comparative purposes. Figures R 6 and R 7 are examples of surfaces exposed to seawater of 1/10 and 1/100 normal calcium concentration, respectively.

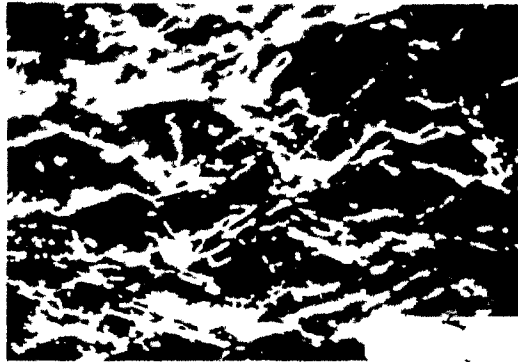
A.IV. Reaction with Fluoride-Spiked Seawater

The electron micrographs of Mexican apatite surfaces exposed to seawater of 1000 ppm NaF spike (1 atm., 2°C, 8 days) showed a large number of square-shaped crystals, similar to the structure of calcium fluoride. (Figures R 8 I, II).

After exposure to seawater spiked to 1000 ppm NaF, a few rod-shaped crystals were noted (Figure R8II e,f). These were not as abundant, nor as long, as the rods seen on the surface exposed to regular seawater. The small number and size suggests that the presence of the adsorbed and/or incorporated fluoride inhibited the formation of the rods.

Electron micrographs of the marine apatite that was exposed to seawater spiked with 500 ppm NaF (2°C, 8 days) Figure R 9) showed the formation of both hexagonal and flat rectangular crystals. The hexagonal crystals were similar to those identified as apatite on the surface of marine apatite

Figure R6 : Ontario Apatite Exposed to Seawater
Containing 1/10 Normal Calcium Con-
centration in Seawater
(1 atm., 2°C, 8 days)



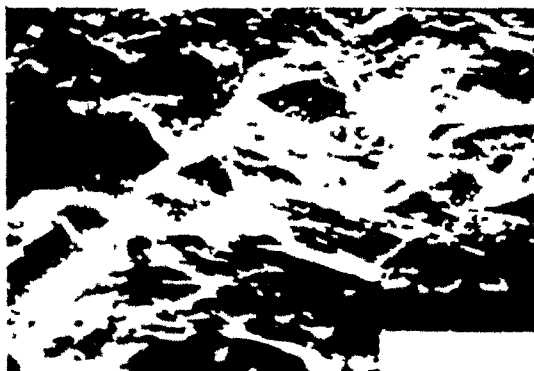
a



b



c



d

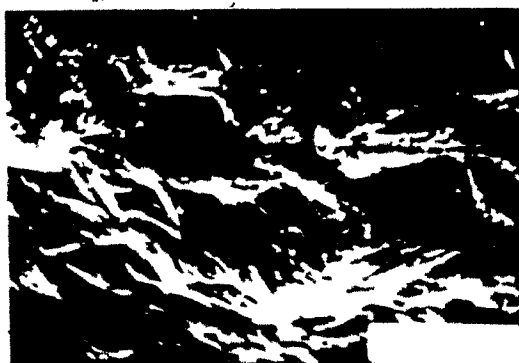


e

Figure R7: Ontario Apatite Exposed to Seawater of
1/100 normal calcium concentration in
Seawater. (1 atm., 2°C, 8 days)



a



b



c

Poor copy

Figure R8: Mexican Apatite Exposed to Seawater
Containing 1000 ppm NaF (1 atm., 2°C, 8 days)



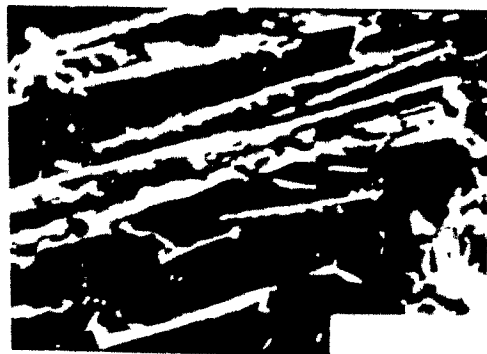
a



b



c



d



e



f



a



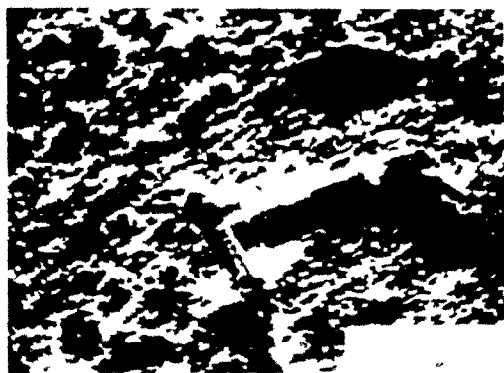
b



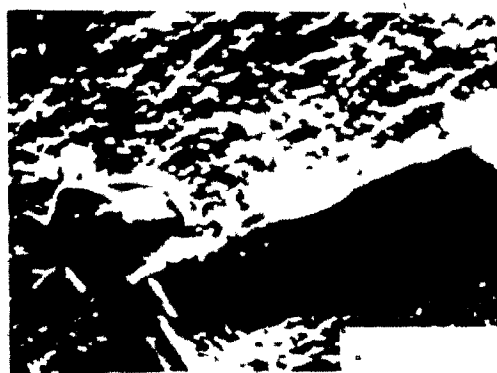
c



d

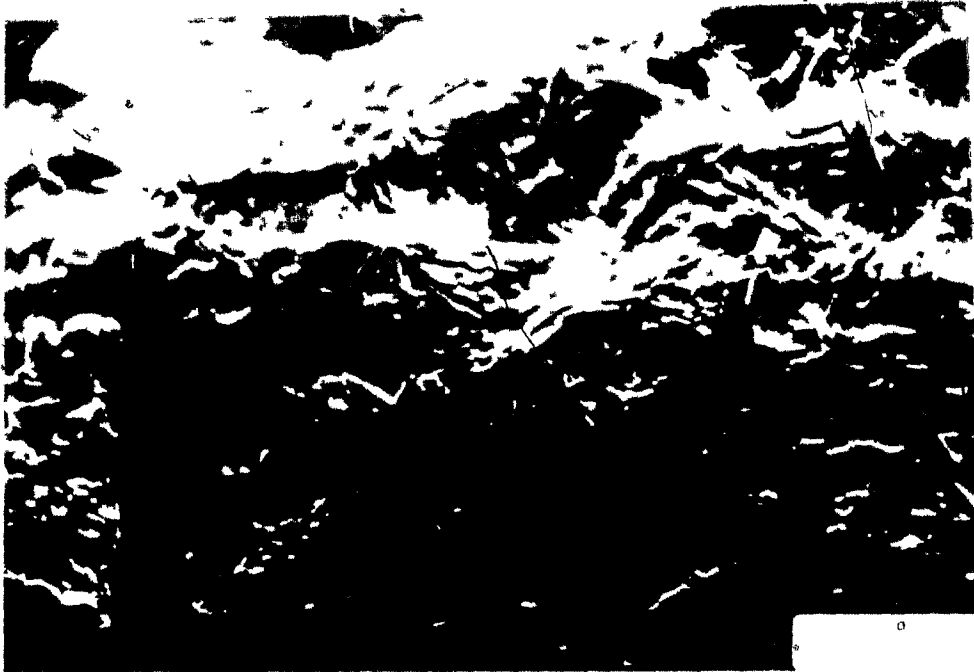


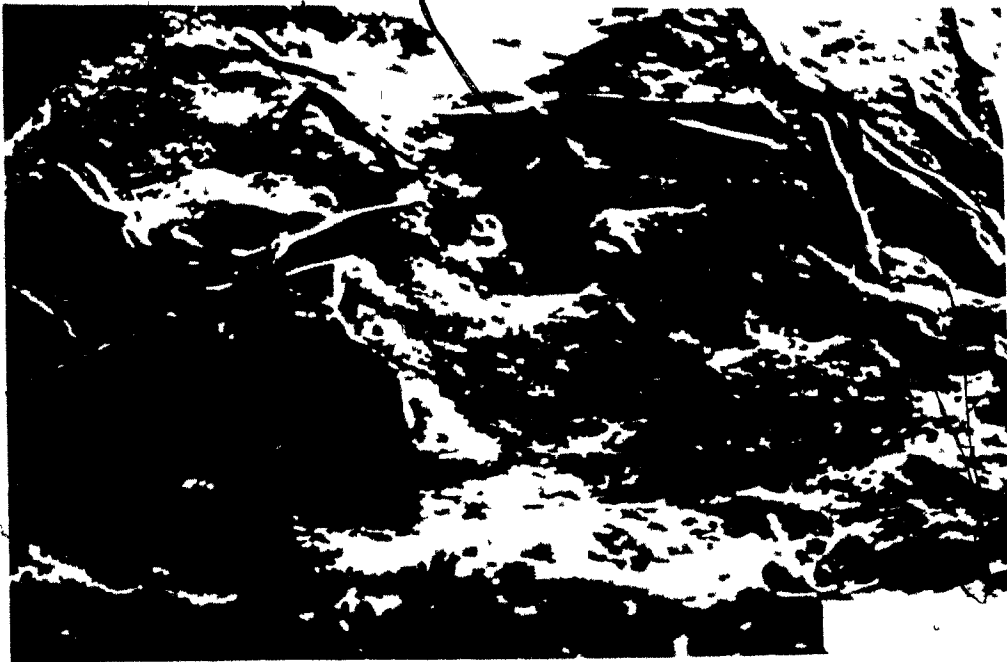
e



f

Figure R9: Marine Apatite Exposed to Seawater
Containing 500 ppm NaF
(1 atm., 2°C, 8 days)





c



d

exposed to regular seawater. The rectangular crystals, although not similar in shape to traditional calcium fluoride crystals, could be a calcium-fluoro-phosphate compound. The high pH (8) and high phosphate content should tend to cause a preferential formation of an apatite.

Surfaces of Mexican apatite which had been first exposed to seawater spiked with 500 ppm NaF and then exposed to regular seawater (1 atm., both for eight day periods) still exhibited square/rectangular crystals seen on the surface just exposed to fluoride-spiked seawater (Figure R13).

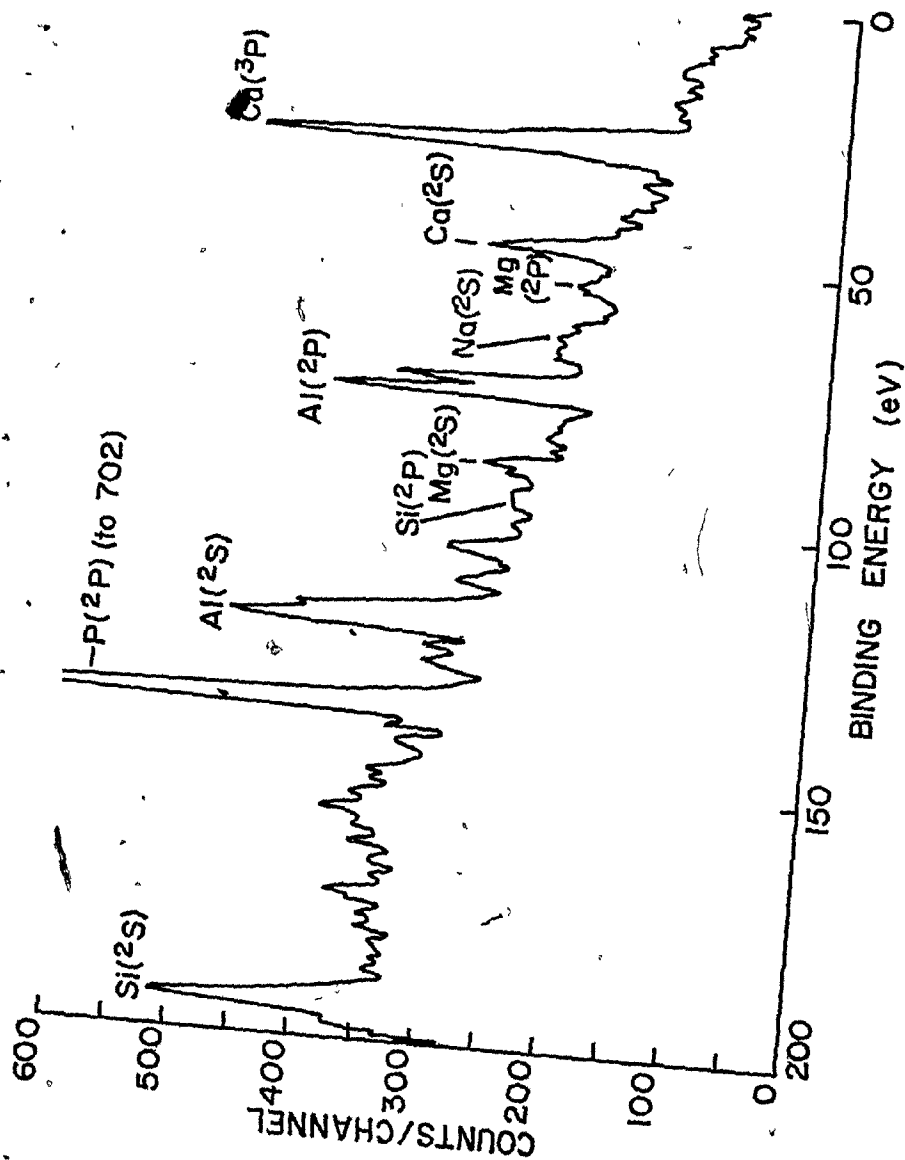
Figures R10 & R12 show ESCA scans of unexposed Mexican and Ontario apatites. Also shown are the ESCA widescans of the Mexican, Marine and Ontario apatite surfaces exposed to seawater spiked with 500 ppm NaF. After argon ion-etching of the apatite surface exposed to seawater spiked with fluoride, the ESCA scan for fluoride showed a significant decrease in peak height. This indicates that the apatite has experienced an uptake of fluoride on the surface. Alteration in the size of the calcium peaks also indicates a change in chemical composition of the surface.

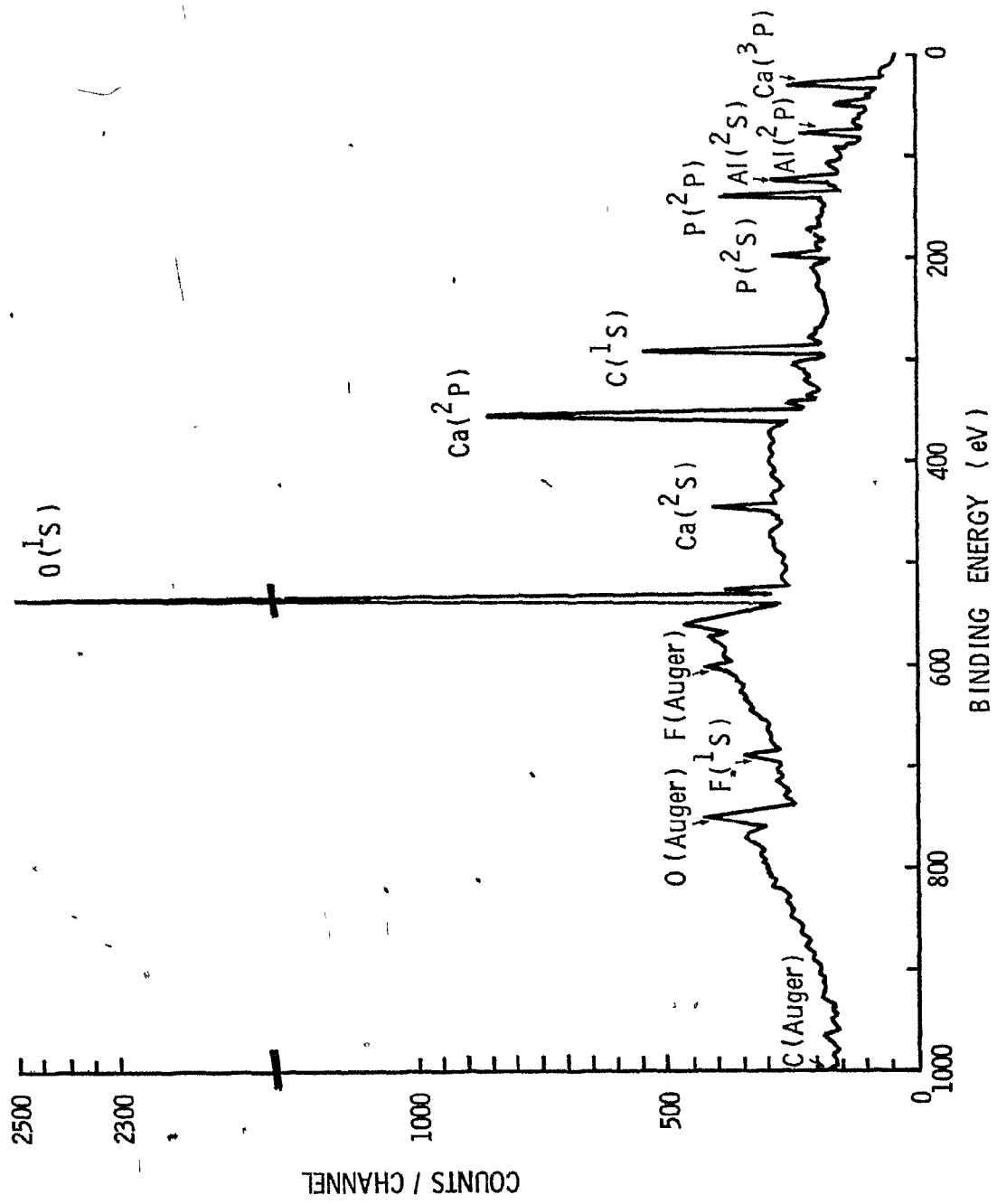
B. Reaction With Seawater at Elevated Pressures

B.I. Reaction With Unspiked Seawater

Mexican, Ontario, and marine apatites were exposed to unspiked seawater at various pressures: 125 atm. (Mexican,

Figure R10: ESCA scan I. Unexposed Mexican Apatite
II. Mexican Apatite Exposed to
Seawater Containing 500 ppm
NaF (1 atm., 2°C, 8 days)





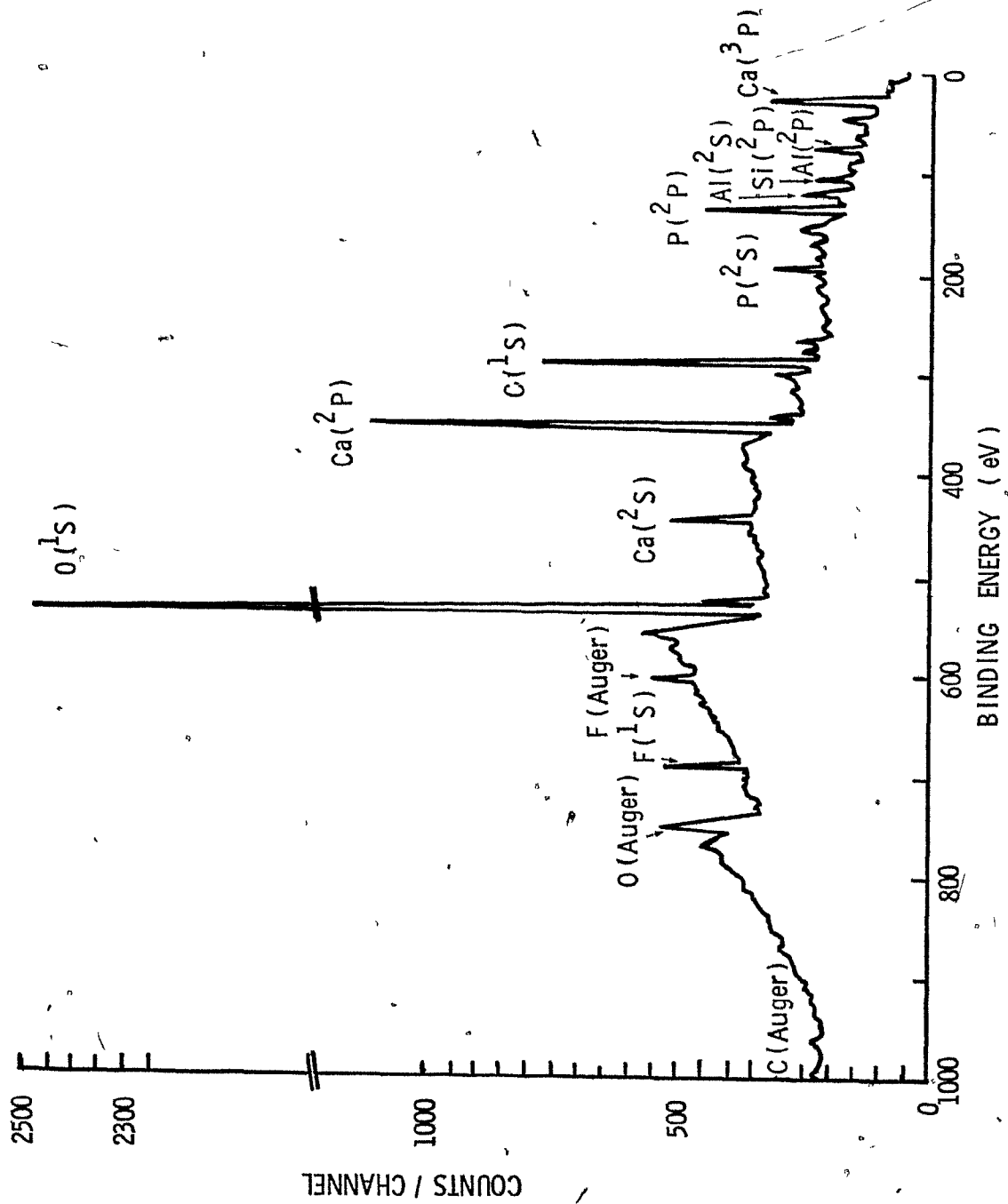


Figure R11: ESCA Scan of Marine Apatite Exposed to
Seawater Containing 500 ppm NaF
(1 atm., 2°C, 8 days)

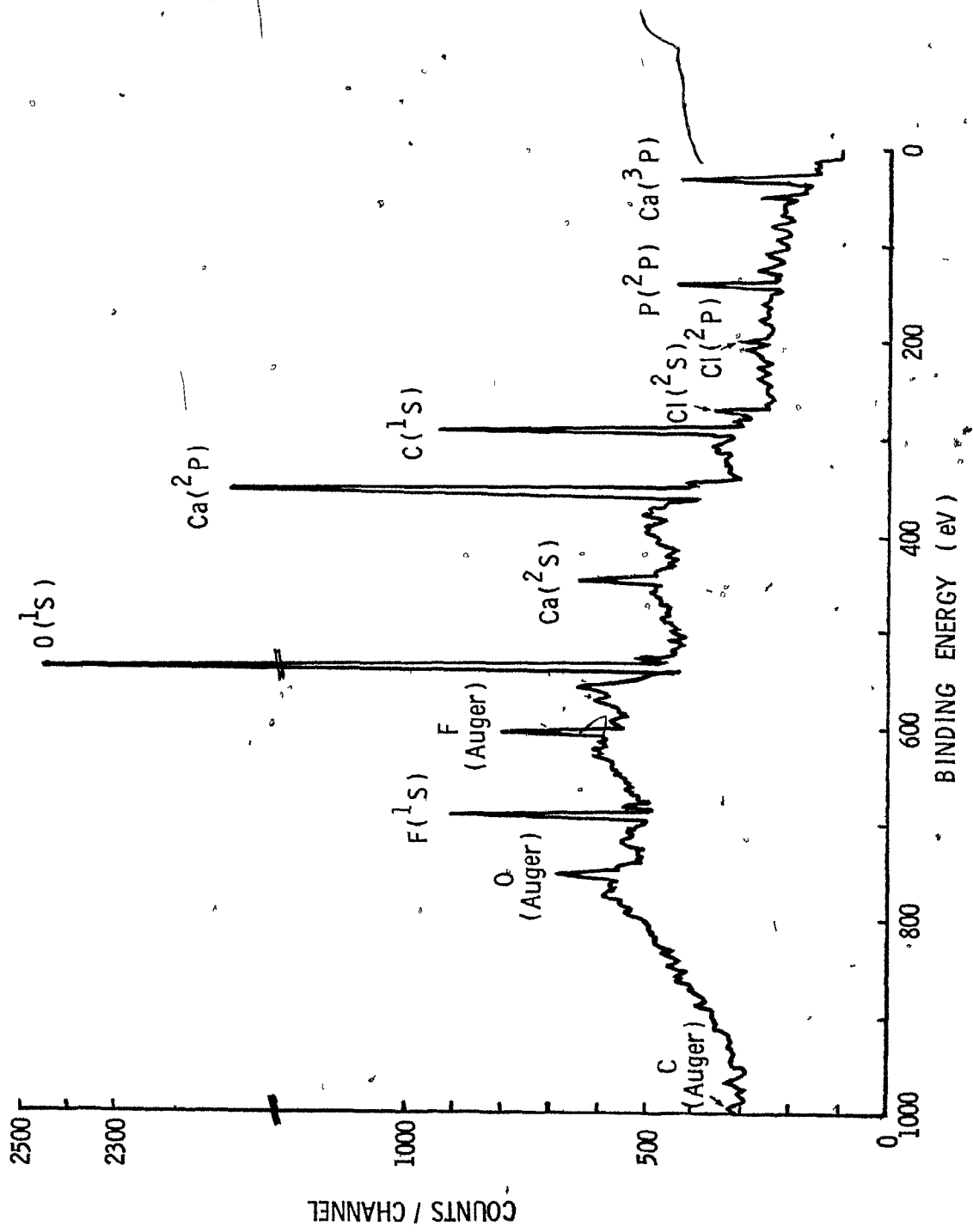
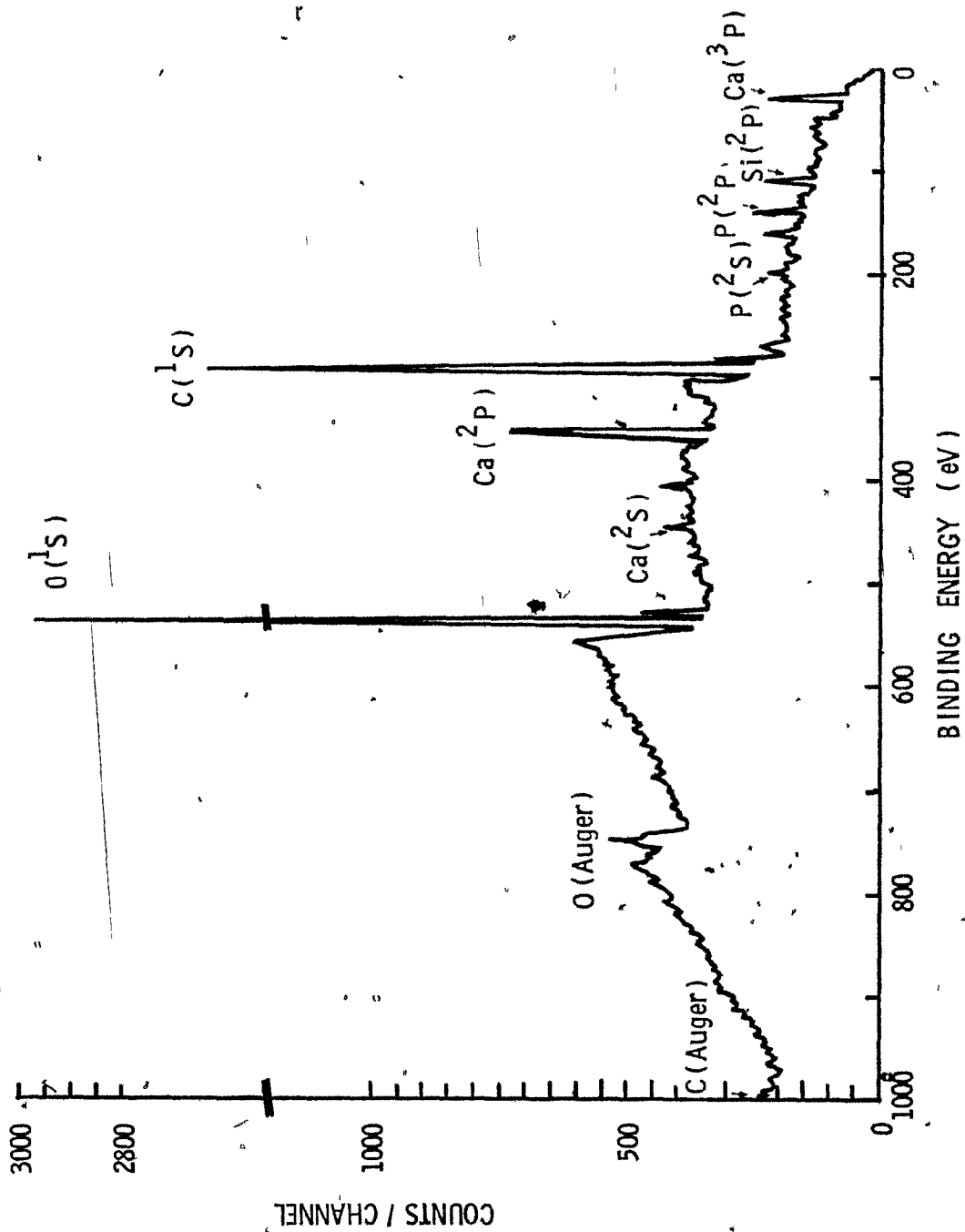


Figure R12: ESCA scan I. Unexposed Ontario Apatite
II. Ontario Apatite Exposed to
Seawater 500 ppm NaF
(1 atm., 2°C, 8 days)



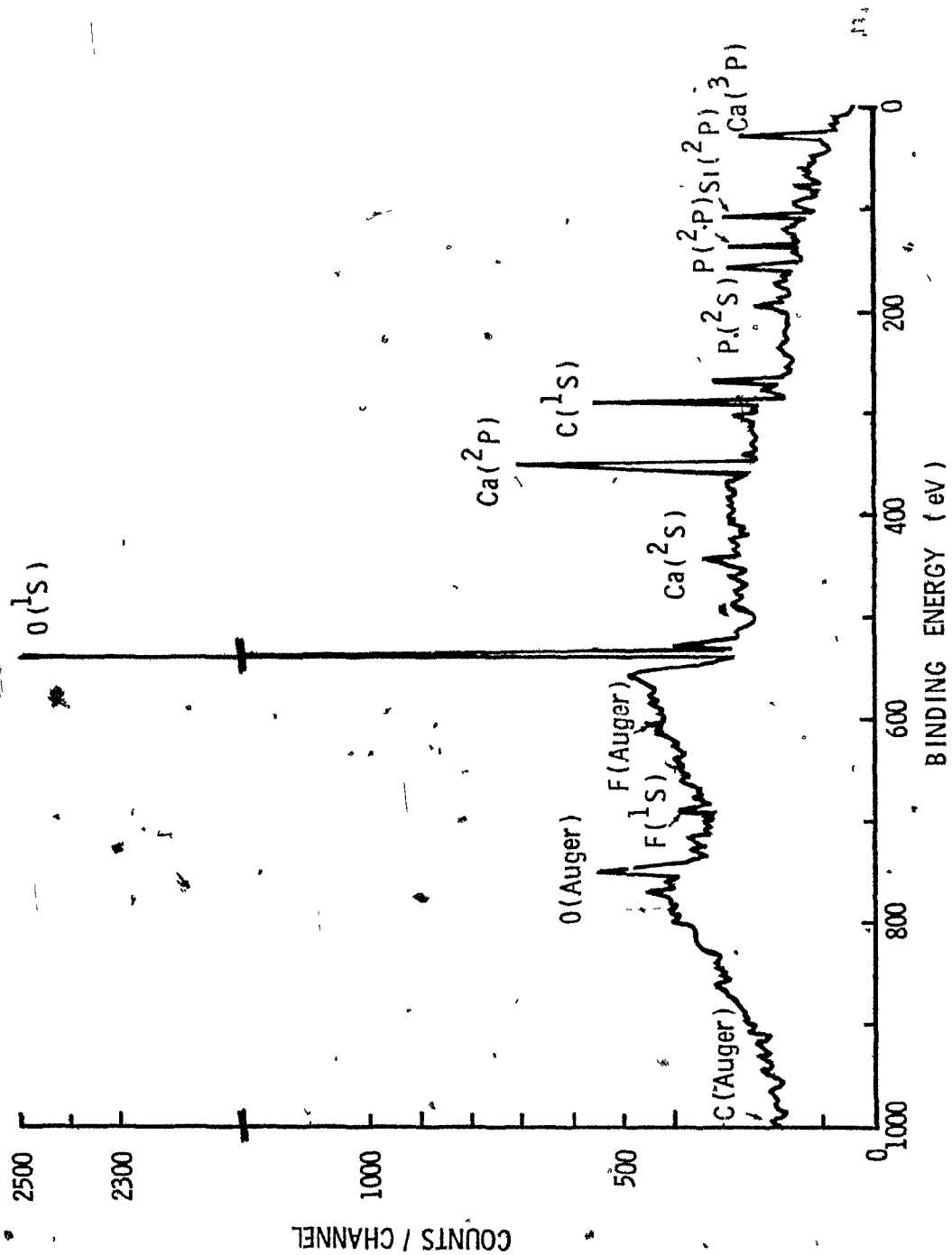


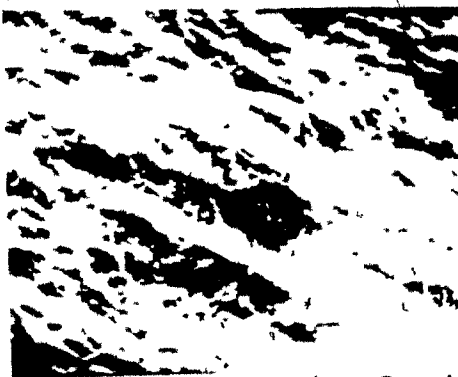
Figure R13: Mexican Apatite Pretreated in Seawater
Containing 500 ppm NaF Exposed to Regular
Seawater (1 atm., 2°C, 8 days for each
period)



a



b



c



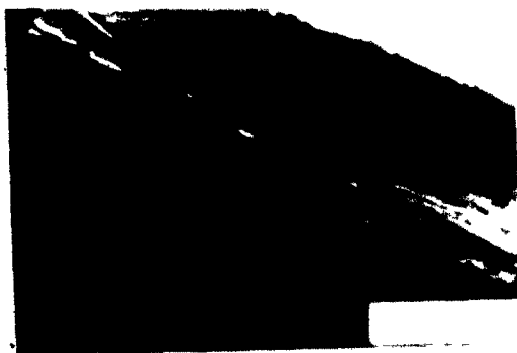
d

5°C, Figure R14), 250 atm. (Mexican, 25°C, Figure R15), 500 atm. (Mexican, 5°C, Figure R15), 710 atm. (Mexican, 5°C, Figure R16), 1000 atm. (Mexican, 5°C, Figure R17; Ontario, 25°C, Figure R18; Marine, 25°C, Figure R19) (each reaction for four days). Electron micrographs showed distinct rod-shaped crystals in great abundance on all the surfaces. These were similar to the rod-shaped crystals seen on the surface of Mexican apatite exposed to seawater at 1 atmosphere. The rods were about 4 microns in diameter and up to 400 microns long (Figure R15c, e).

ESCA analyses were performed on Ontario, Mexican (Figure R20) and Marine apatites exposed to seawater at 1000 atm. and the Mexican apatite exposed at 125 atm. (Figure R21). The analyses of the Mexican apatite exposed at 1000 atm., showed the appearance of a Si (^{2}P) peak and the virtual disappearance of the Al (^{2}S and ^{2}P) peaks. There was also an increase in the Mg (^{2}S and ^{2}P) and the Ca (^{3}S) peaks. The increased concentration of magnesium indicated that increased pressure promoted the exchange of magnesium for calcium within the crystal lattice. The increased magnesium content would yield a more soluble apatite.

The Marine sample showed a high level of Si in the unreacted sample and essentially no change in the reacted sample. The Ontario apatite showed a low background of Si, Al and Mg in the unexposed sample and showed little change when exposed to solution. There was some increase in the Ca (^{3}S).

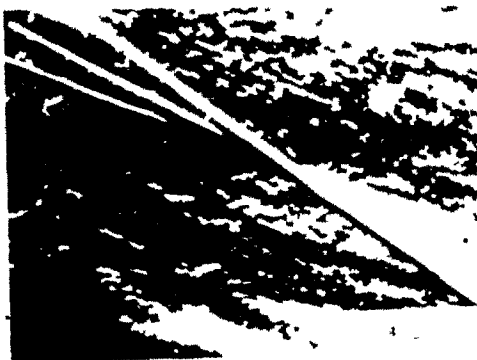
Figure R14: Mexican Apatite Exposed to Seawater with
the System at 125 atmospheres
(5°C, 4 days)



a



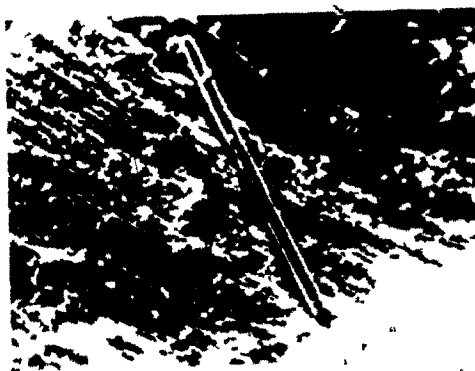
b



c



d



e



f

Figure R15: Mexican Apatite Exposed to Seawater
with the System at -
250 atmospheres (25°C, 4 days) a - d
500 atmospheres (5°C, 4 days) e, f



a



b



c



d



e



f

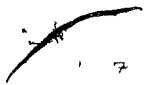


Figure R16: Mexican Apatite Exposed to Seawater with
System at 710 atmospheres (5°C, 4 days)

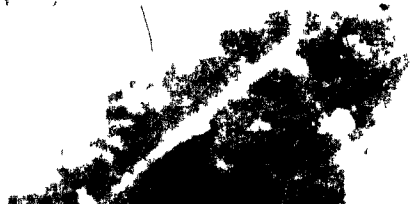
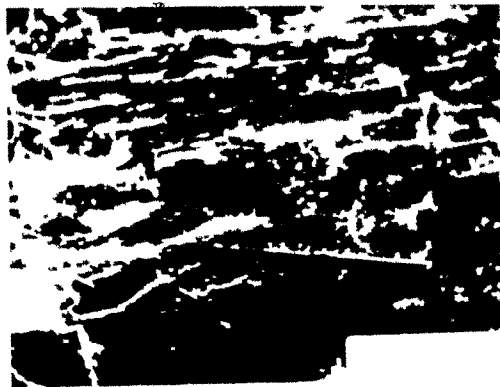


Figure R17: Mexican Apatite Exposed to Seawater with
the System at 1000 atmospheres (5°C, 4 days)



a



b

d



e



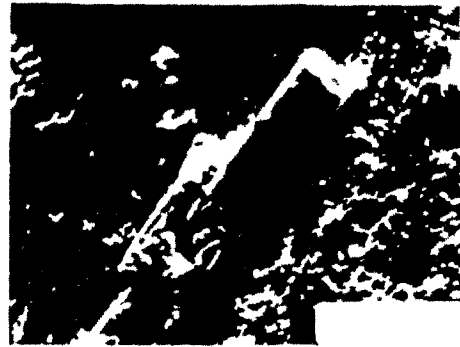
c



f



a



d



b



e



c



f

52a

Figure R18: Ontario Apatite Exposed to Seawater with
the System at 1000 atmospheres (5°C, 4 days)



a



b



c

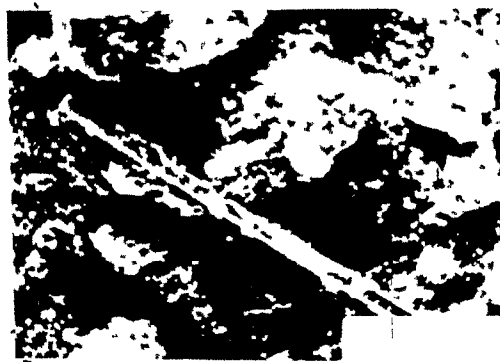
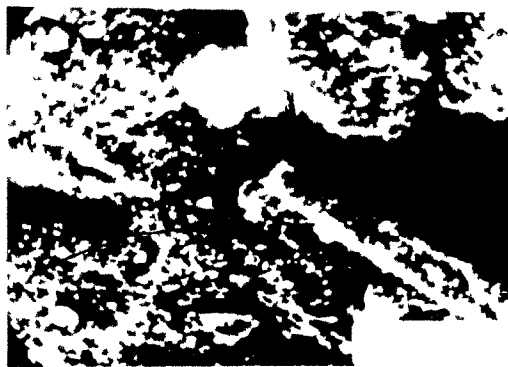
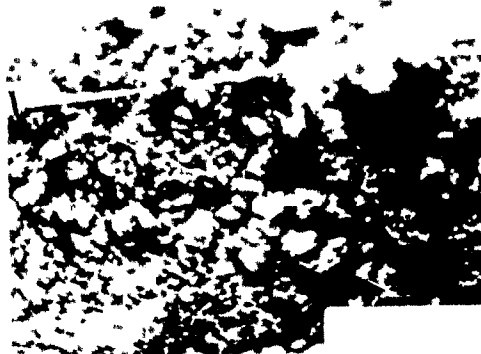
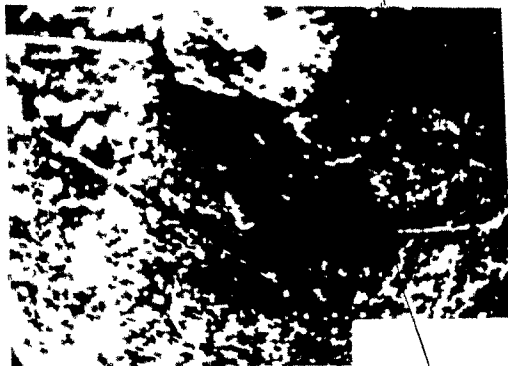


d



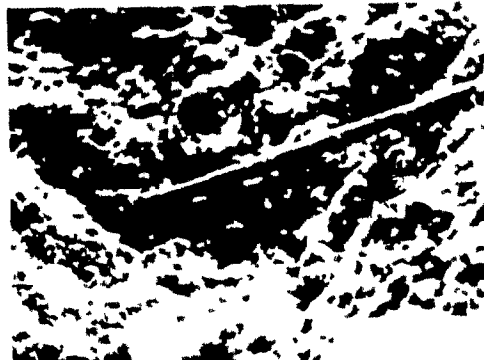
e

Figure R19: Marine Apatite Exposed to Seawater with the System at 1000 atmospheres (5°C , 4 days)
The large crystal in Ib, and more closely shown in Ic and d is similar to crystals seen in unexposed samples of marine apatite. Note similarity to crystals formed during experiment (lower section Ia, also II)





a



d



b



e



c



f

Figure R20: ESCA Scan of Mexican Apatite Exposed
to Seawater with the System at 1000
Atmospheres (5°C, 4 days)

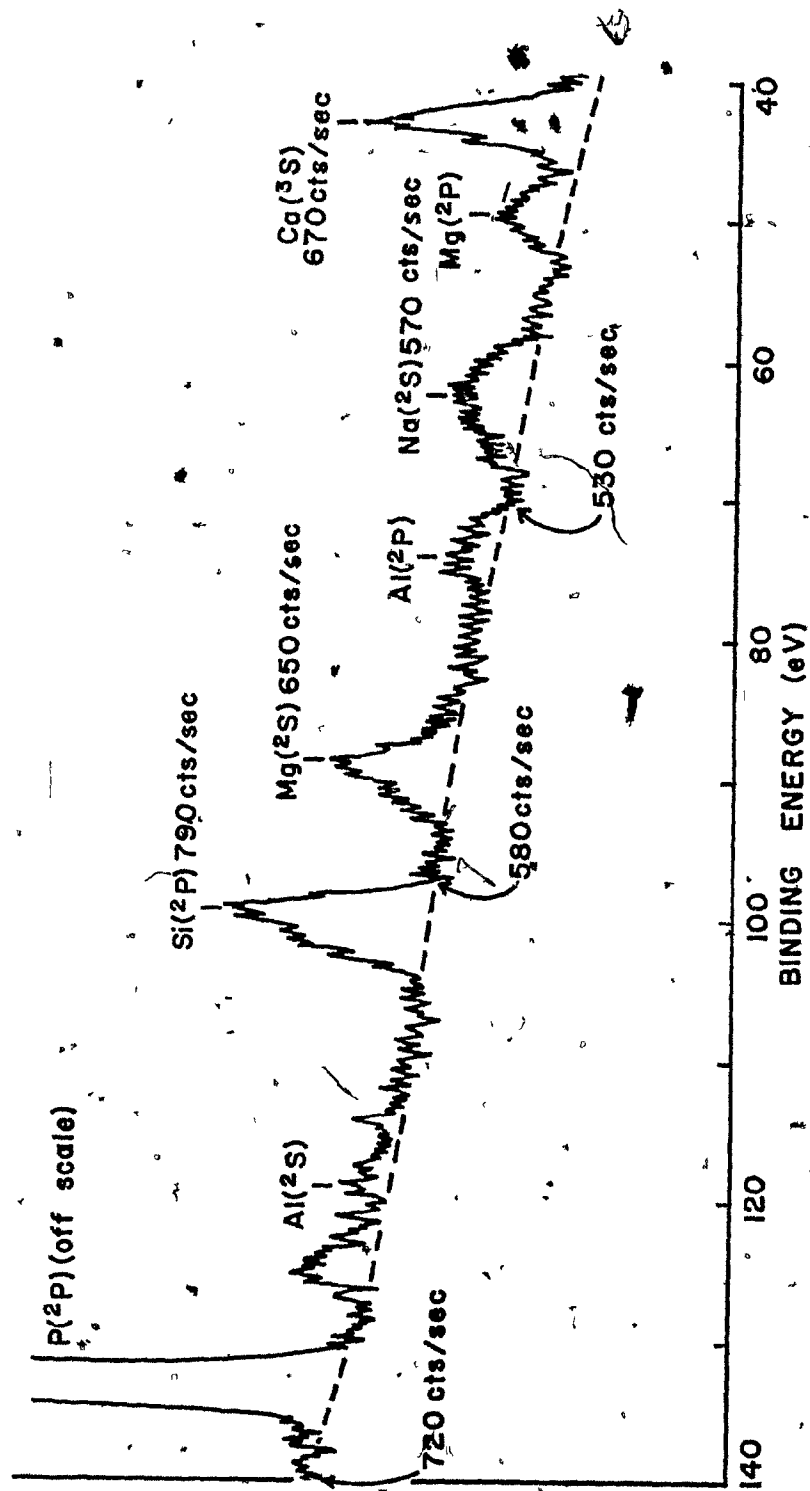
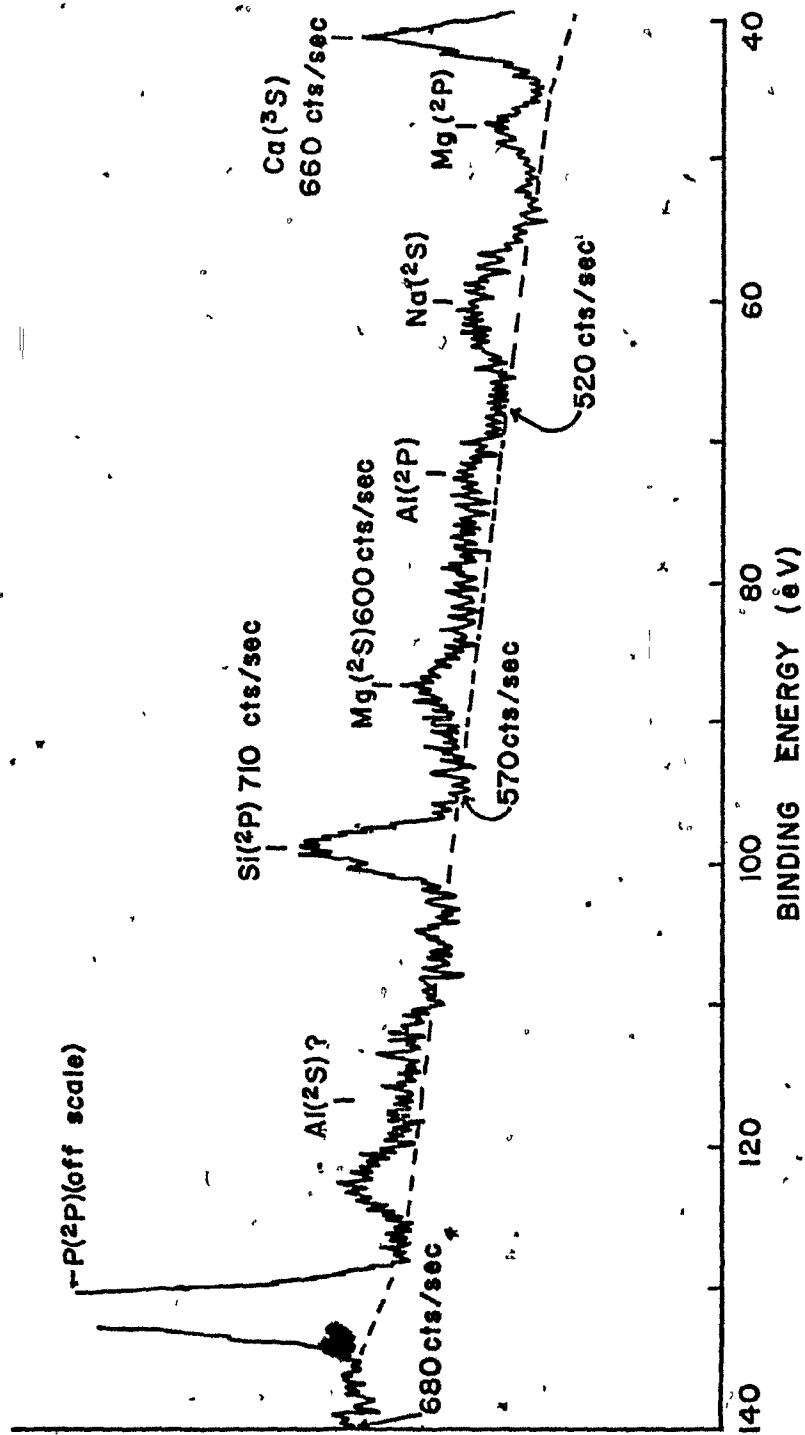


Figure R21: ESCA Scan of Mexican Apatite Exposed
to Seawater with the System at 125
Atmospheres (5°C, 4 days)



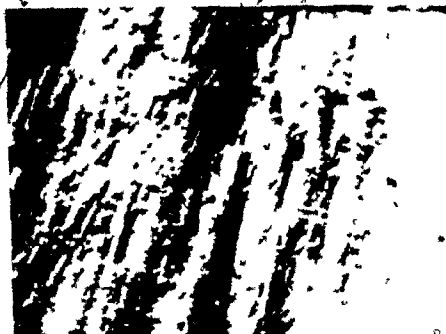
The ESCA analysis of the Mexican surface exposed to seawater at 125 atm. showed less uptake of Si or Mg than the surface exposed at 1000 atm. Pressure obviously promotes exchange and other chemical reactions. The change in the peak sizes for the ions of the apatite crystal indicates a change in the bonding and composition of the surface layer examined by the ESCA, that is, alteration of the apatite surface when exposed to seawater occurred.

Energy dispersive analyses of the rod-shaped crystals indicated a high Si content, but a complete quantitative analysis was not possible.

B.II. Reaction with Fluoride-Spiked Seawater

Samples of Mexican apatite were exposed to seawater spiked with 500 ppm NaF at various pressures: 1000, 710, 500 and 128 atm., for four days at 5°C. Electron micrographs (Figures R22,23) of the surfaces showed no square-shaped crystals similar to those seen on surfaces exposed to fluoride-spiked seawater at 1 atm. However, a small number of rod-like crystals were observed. As with the 1 atm. results, the rods were small in size and in number. Only three rods were observed on the Mexican apatite exposed to fluoride-spiked seawater at 1000 atm., compared to the very large number observed on the surface exposed to unspiked seawater. The absence of square-shaped crystals could be due to their

Figure R22: Mexican Apatite Exposed to Seawater
Containing 500 ppm NaF with the System at
125 atmospheres (5°C, 4 days) a - c
500 atmospheres (5°C, 4 days) d, e



a



b



c



d



e

Figure R23: Mexican Apatite Exposed to Seawater
Containing 500 ppm NaF with the System at
1000 atmospheres (5°C, 4 days) a - c
710 atmospheres (5°C, 4 days) d - f

Handwritten symbol resembling a stylized '8' or a loop.

Handwritten number '1'.



a



b



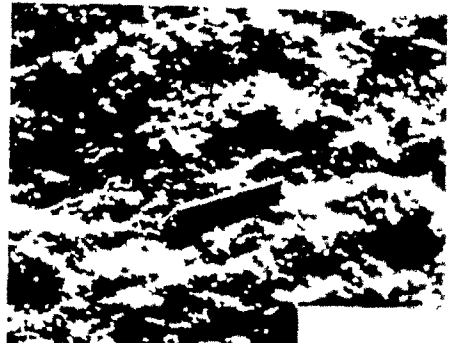
c



d



e



f

Handwritten symbol resembling a stylized '8' or a loop.

dissolution under the effects of high pressure. The presence of the high concentration of fluoride in solution could also have created conditions which interfered with the formation of the tubular crystals.

ESCA analyses of the Mexican apatite exposed to fluoride-spiked seawater at 1000 (Figure R24) and 128 atm. (Figure R25) showed that there was less tendency for the surface to take up Si or Mg compared to the surface exposed to regular seawater at pressure. The fluoride concentration on the surface increased significantly. This increased concentration may have inhibited the uptake of other ions from solution. This can also be seen in the electron micrographs, where the rod-like structures seen on the surfaces exposed to regular seawater were greatly reduced in frequency of appearance on the surface exposed to the fluoride-spiked seawater.

II. Solution

A. Pressure Variations

A.1. Reaction with NaCl Solutions

As described in the Experimental section, NaCl solutions were allowed to react with three apatites - Mexican, Ontario, and Marine - while the system was maintained at high pressures (30-1000 atm.) and low temperature (5-6°C). After a suitable reaction time had elapsed, the reacted liquid was removed, filtered, and analysed. Graphs of the solution concentrations

Figure R24: ESCA Scan of Mexican Apatite Exposed to
Seawater Containing 500 ppm NaF with the
System at 1000 Atmospheres (5°C, 4 days)

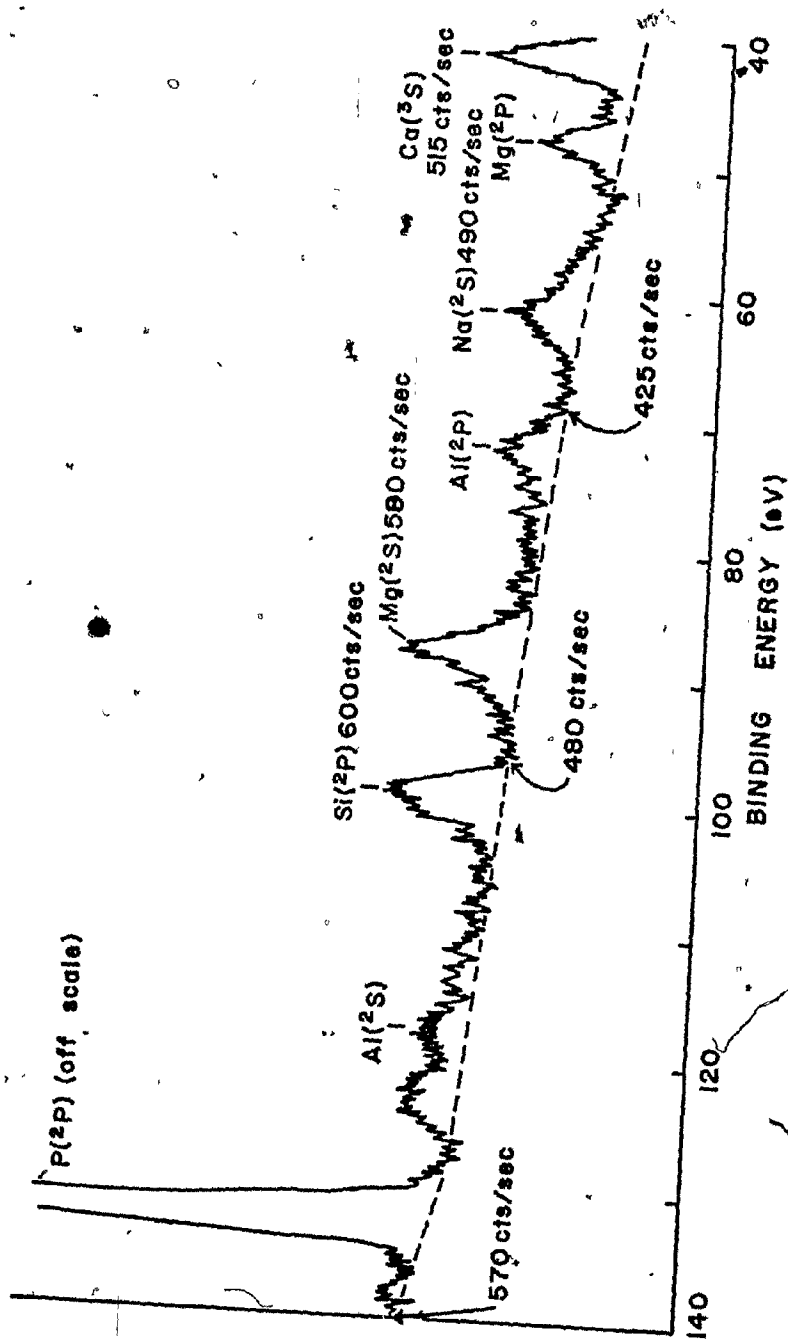
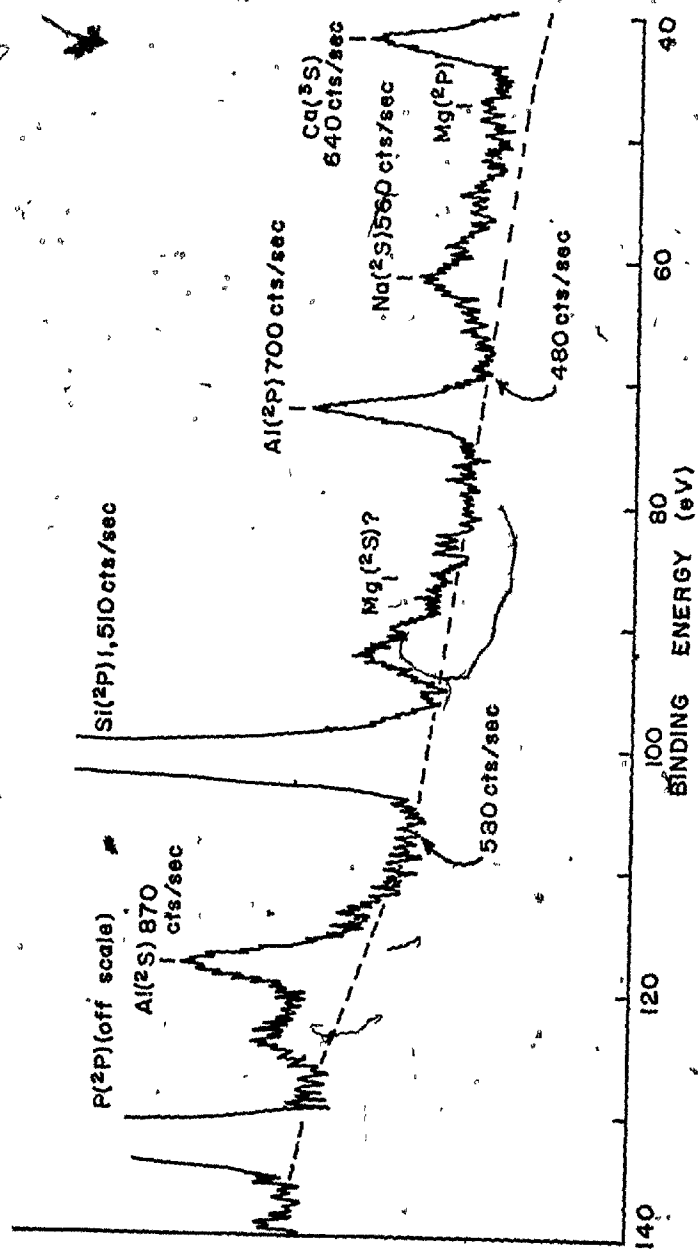


Figure R25: ESCA Scan of Mexican Apatite Exposed to
Seawater Containing 500 ppm NaF with the
System at 125 Atmospheres (5°C, 4 days)



as a function of pressure variation are given in Figures (R26-28). Except for the case of the hydroxyl ion concentration, good least-squares linear correlations were obtained for the concentration variation as the pressure was both increased and decreased. Since pH was not measured within the high pressure vessel, but was measured after the liquid was removed, the hydroxyl ion concentration reported is only an approximation of the concentration that actually occurred at that pressure value.

Sodium chloride solutions were reacted with the apatites under pressure to provide a comparison with effects that were observed when seawater was reacted with the apatites under pressure. The sodium chloride solutions had approximately the same ionic strength as the seawater, but because neither sodium nor chloride ions ion-pair to a significant extent, a reasonably clean picture of the effect of pressure on apatite solubility should have been obtained.

AII. Reaction with Unspiked Seawater

In an experimentally similar manner to the reaction of NaCl solutions with the apatites, seawater was allowed to react with fresh samples of the same three apatites. Graphs of the solution concentrations as a function of pressure variation are shown in Figures R29-R31. In the cases of the Mexican and Ontario apatites good least-squares linear cor-

The Effect of Pressure on the Dissolution
of Apatite in 0.65 N NaCl Solution (5-6°C)

Figure R26: Mexican

R27: Ontario

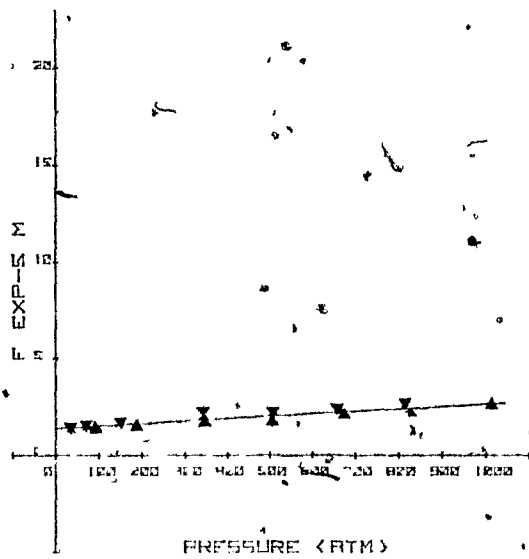
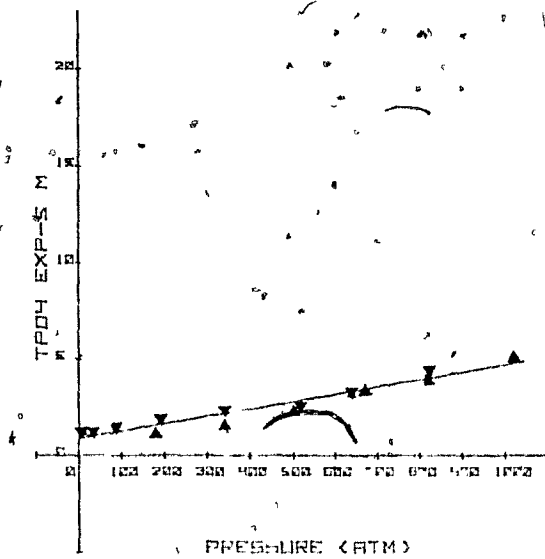
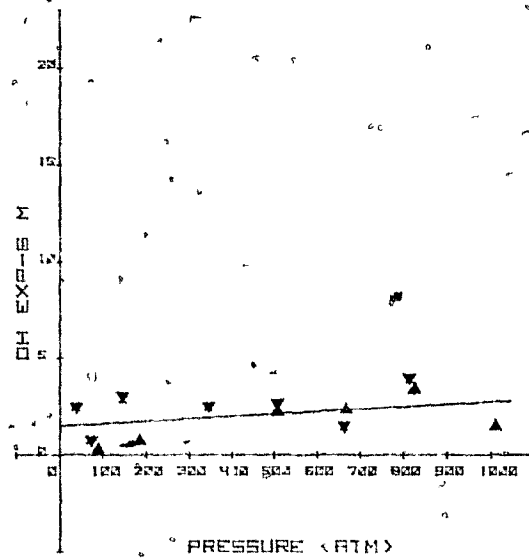
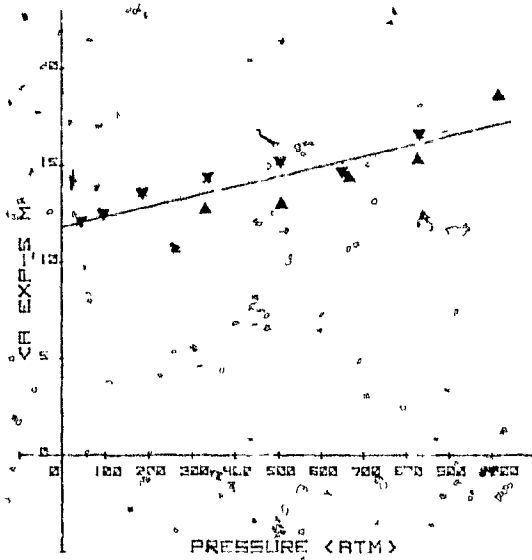
R28: Marine

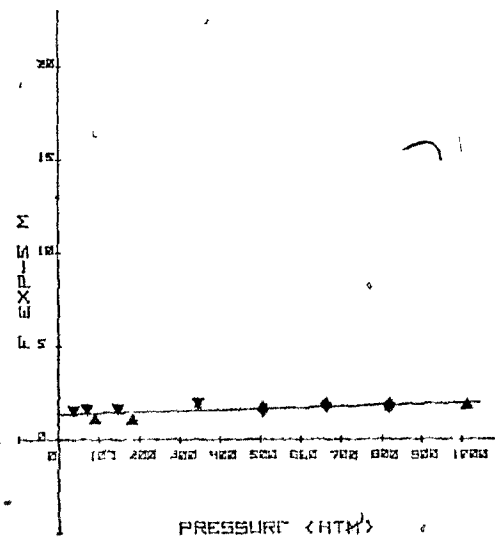
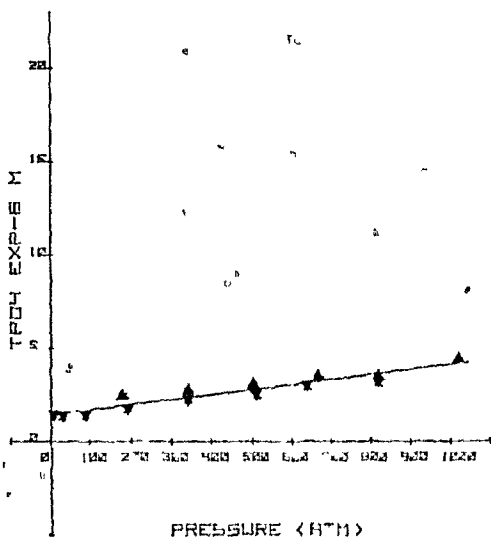
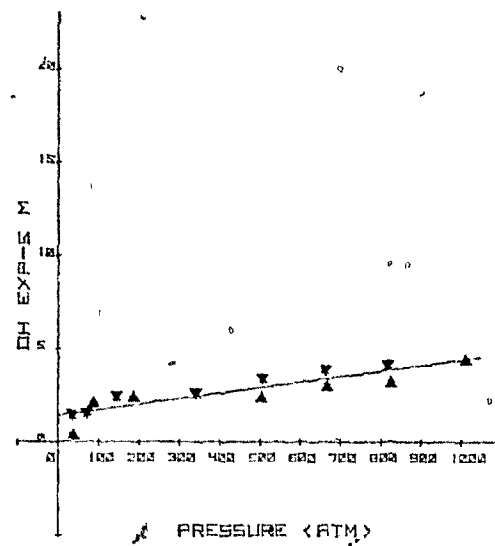
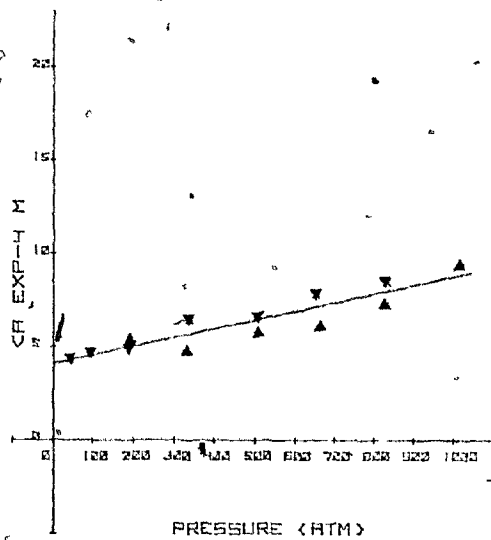
▲: increasing pressure

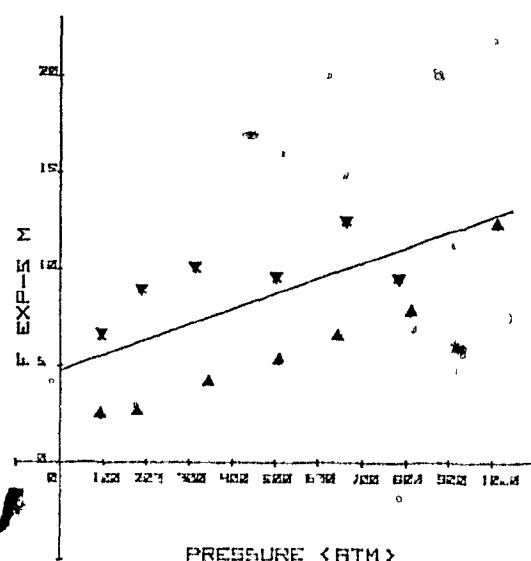
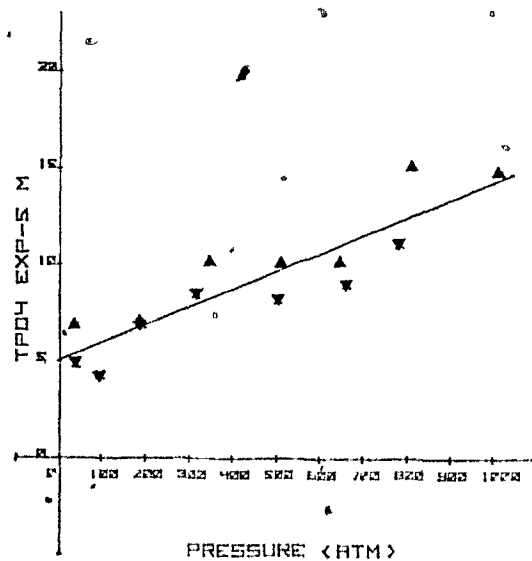
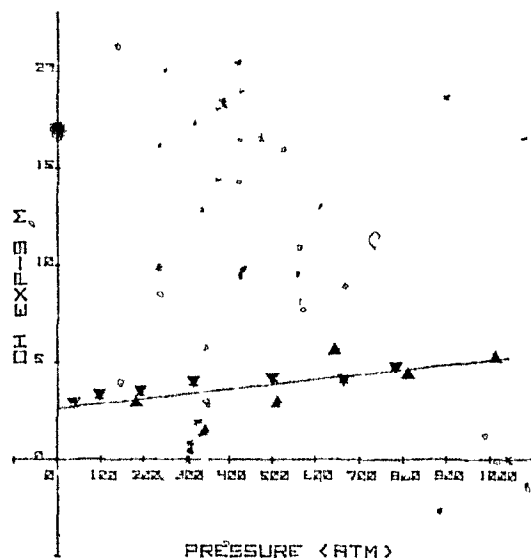
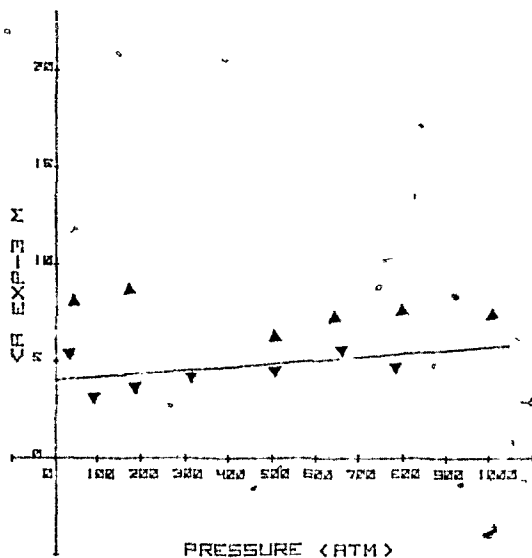
▼: decreasing pressure

◇: common point

*Line is least-squares linear regression.







The Effect of Pressure on the Dissolution
of Apatite in Seawater (5-6°C)

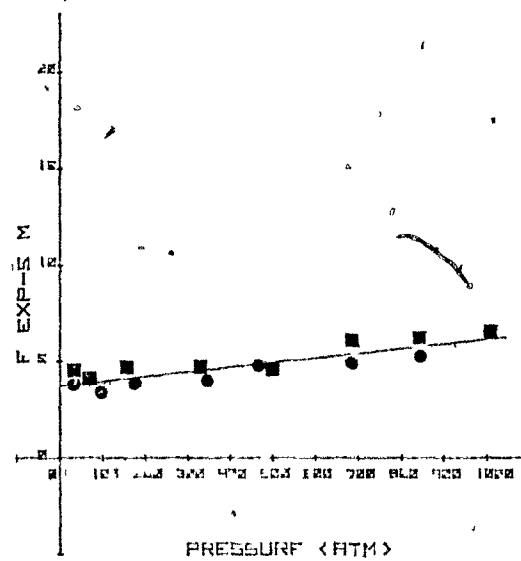
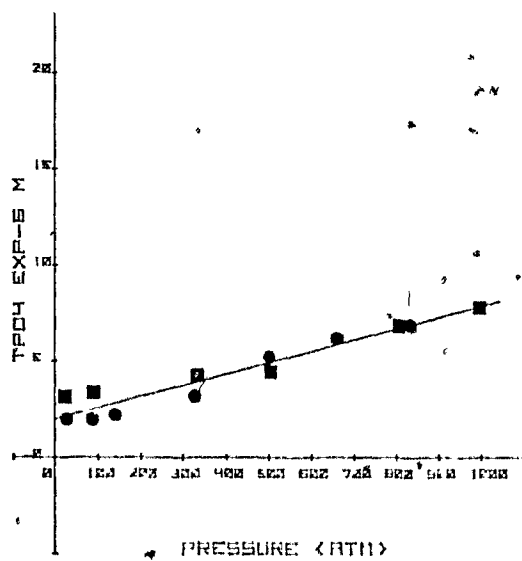
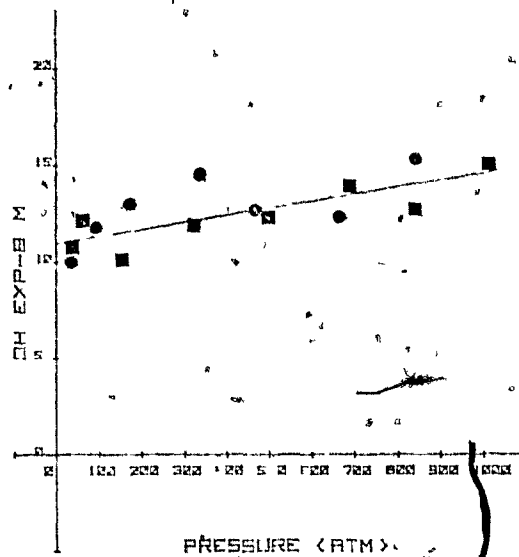
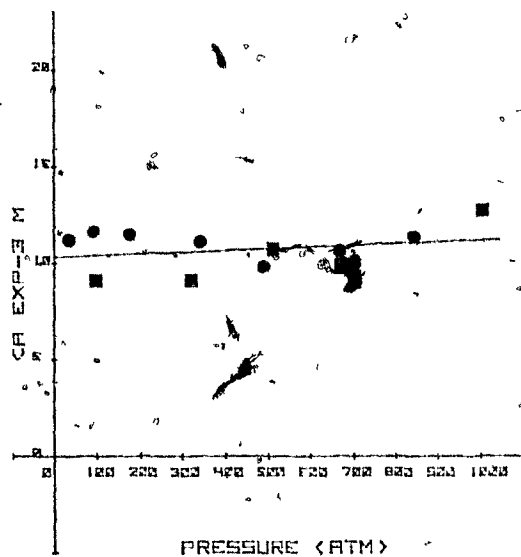
Figure R29: Mexican

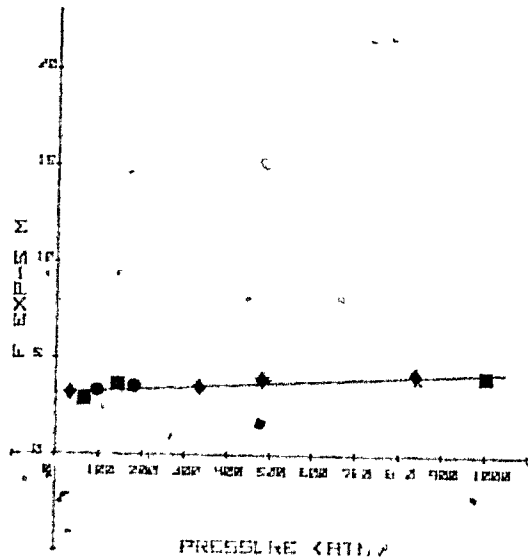
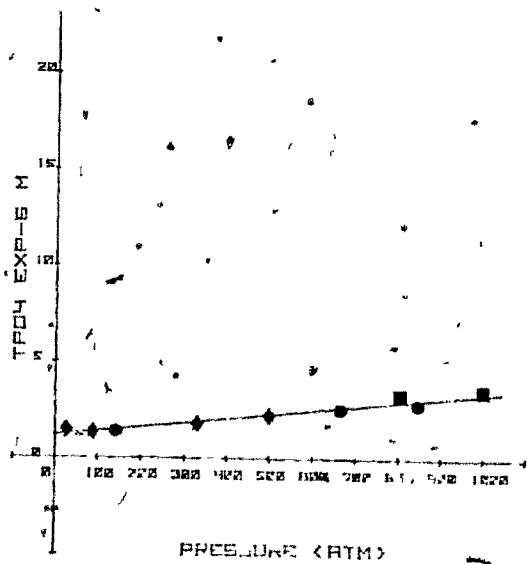
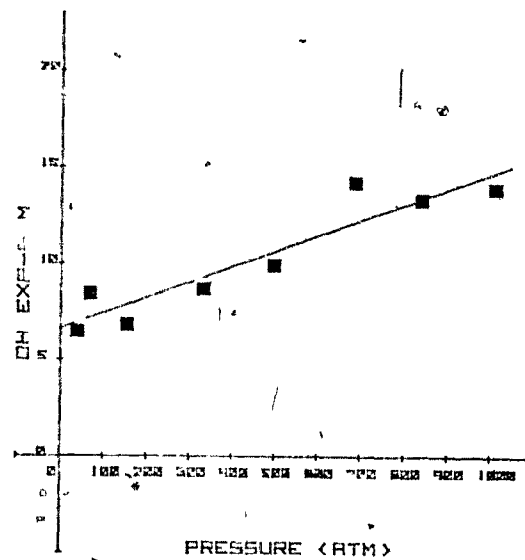
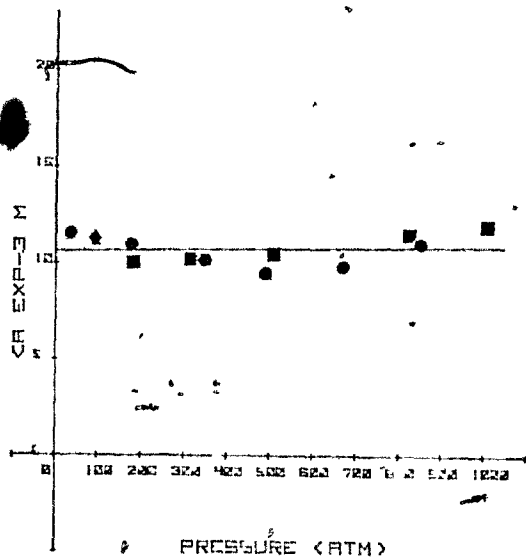
R30: Ontario

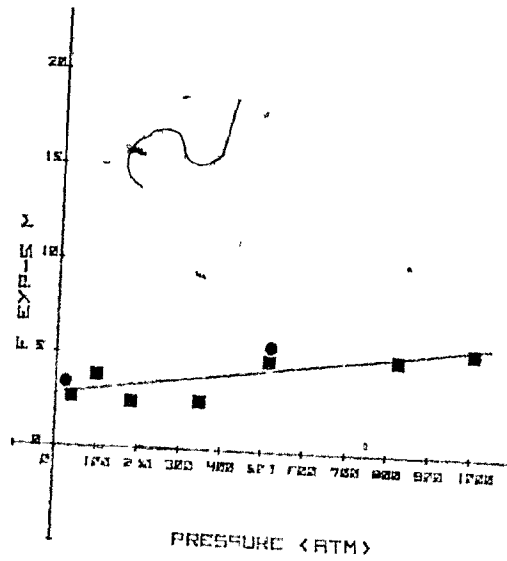
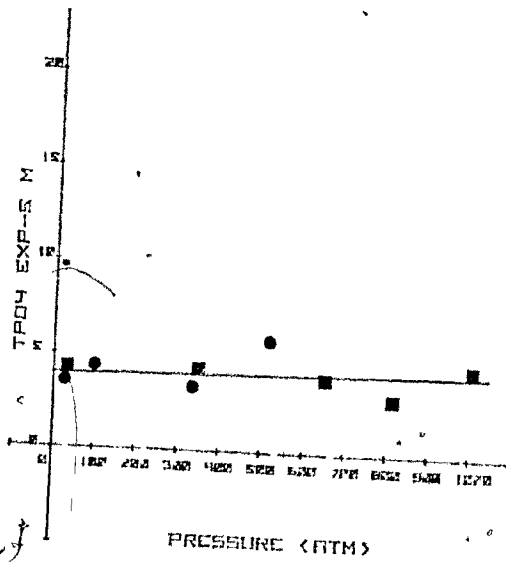
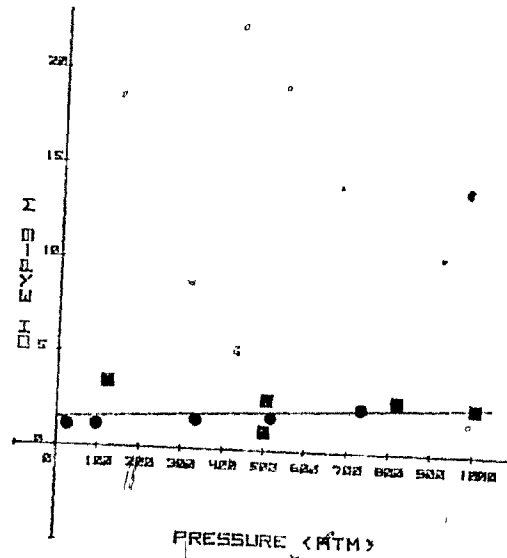
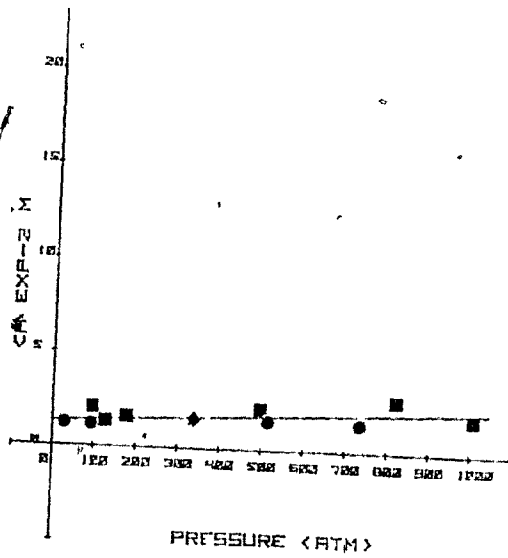
R31: Marine

- : increasing pressure
- : decreasing pressure
- ◇ : common points

Line is least-squares linear regression







relations with pressure variation, as it was increased and decreased, were obtained.

The variation of total phosphate concentration in solution with variation in pressure, as it was both increased and decreased, was found to have a good linear least-squares correlation. However, for the cases of the fluoride and calcium concentrations, it was noted that the linear variation in concentration as pressure was increased was different from the linear variation as the pressure decreased. This variation in response to pressure changes could be due to the presence of CaCO_3 within the marine apatite. The response of the carbonate to pressure changes could interfere with the phosphorite response and mask the "true" apparent solubility.

A.III. Reaction with Fluoride-Spiked Seawater

As described previously, seawater spiked with 500 ppm NaF was reacted with marine apatite as the system was maintained at high pressures. Graphs of solution concentrations as functions of pressure are given in Figure R32. Reasonable least-squares linear correlations of concentration to pressure variation, as pressure was both increased and decreased, were obtained.

A.IV. Comparison of Reaction Solutions

Comparative graphs of the response of total phosphate

The Effect of Pressure on the Dissolution
of Apatite in Seawater Spiked to 500 ppm
NaF (5-6°C)

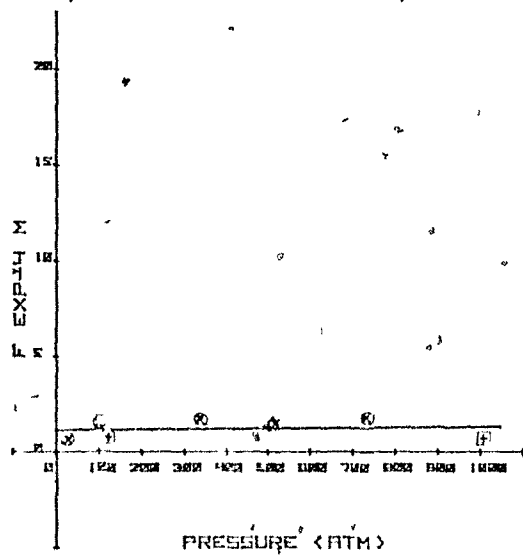
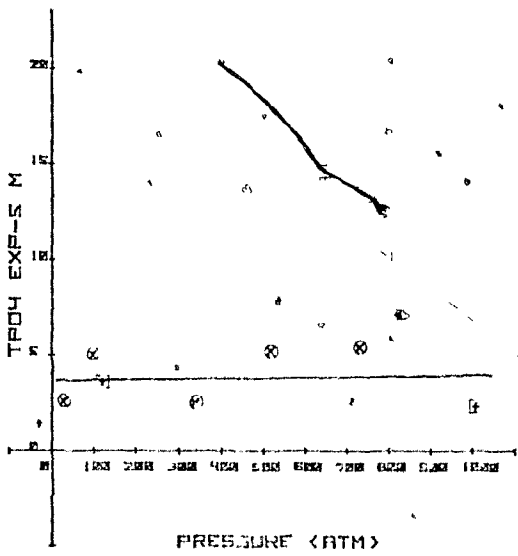
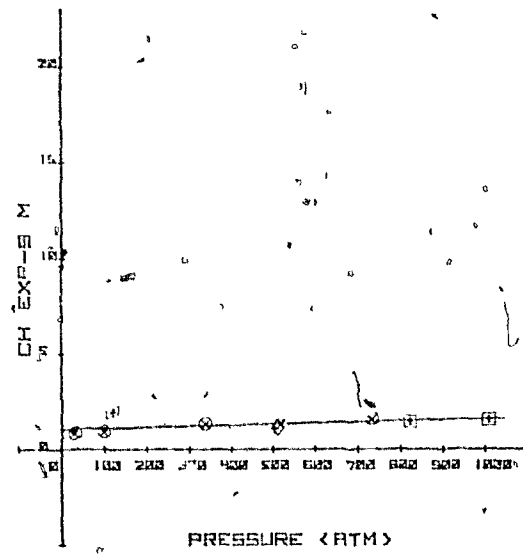
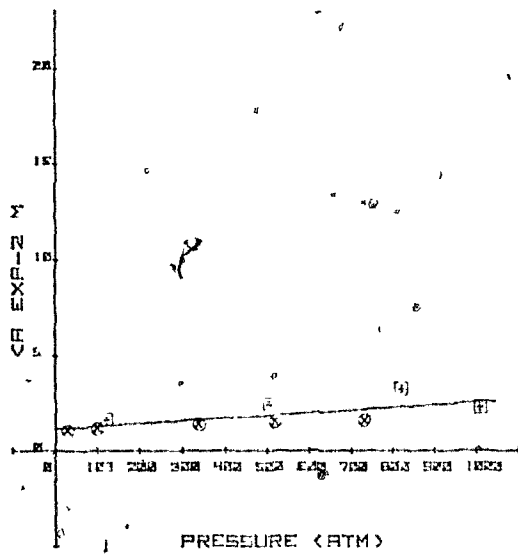
Figure R32: Marine

⊞: increasing pressure

⊗: decreasing pressure

⋈: common point

Line is least-squares linear regression.



concentrations in NaCl and seawater solutions to pressure variations for each of the three apatites are given in Figure R33-R35. Although the common ion effect predicts that the solubility should be greatly decreased in seawater compared to NaCl solutions, it can be readily seen that this is not the case. It is postulated that the effect of ion-pairing in seawater with the constituents, especially the phosphate and fluoride species, contributes to the increased solubility in seawater. This will be more fully discussed in the Discussion section.

B. Temperature Variations

B.I. Reaction with NaCl Solutions

The solubilities of Ontario, Quebec, and Mexican apatites were determined in NaCl solutions at 2° and 25°C (1 atm., 8 days). The graphs of concentration variation as a function of time for the two temperatures are shown in Figures R36-R38. In each case the solubility at 2° was greater than at 25°C. This follows the pattern predicted from the results of Kramer (1964) who gave a value for a solubility product constant in seawater of 10^3 (5°) and 10^5 (25°).

B.II. Reaction with Unspiked Seawater

The solubilities of Ontario, Quebec, Mexican, and Florida apatites were tested in seawater at 2 and 25°C (8

Comparison of the Effect of Pressure on the
Dissolution of Apatite in Seawater to
Dissolution in 0.65N NaCl Solution (5-6°C)

Figure R33: Mexican

R34: Ontario

R35: Marine

■ : seawater

▲ : 0.65N NaCl Solution

increasing pressure

● : seawater

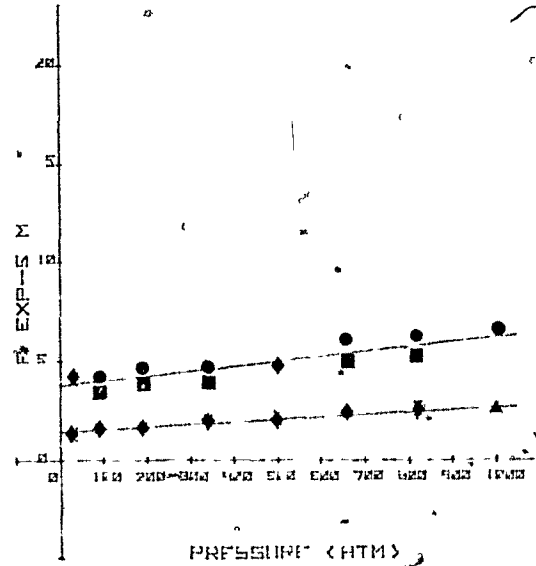
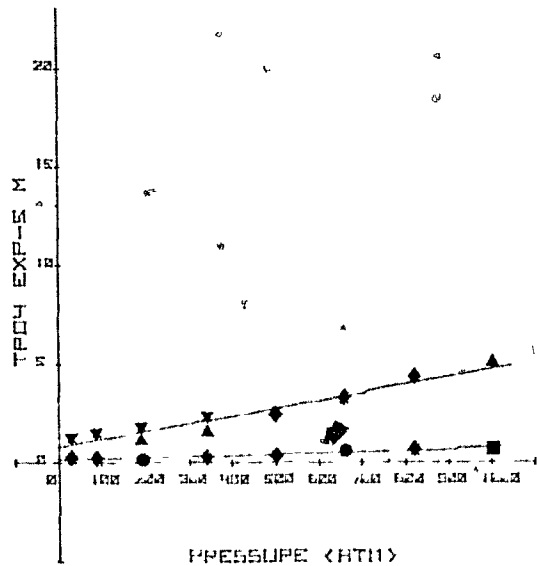
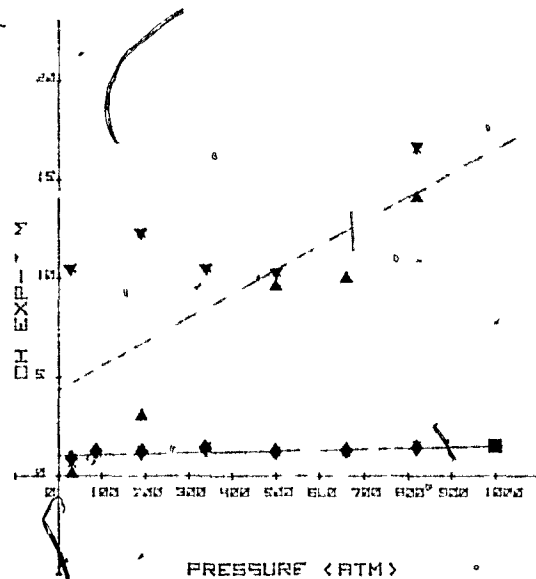
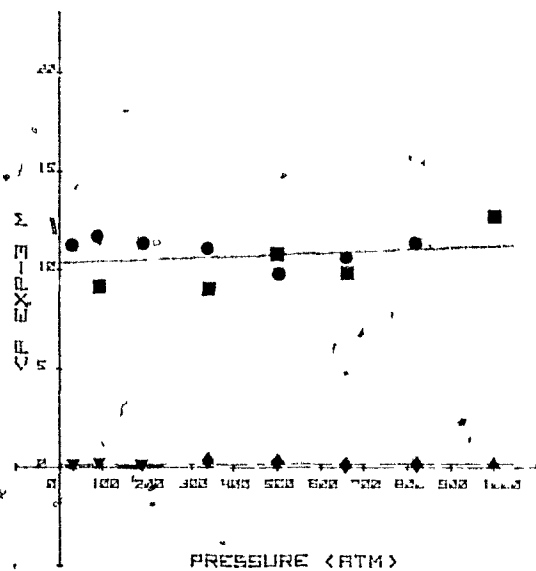
▼ : 0.65N NaCl Solution

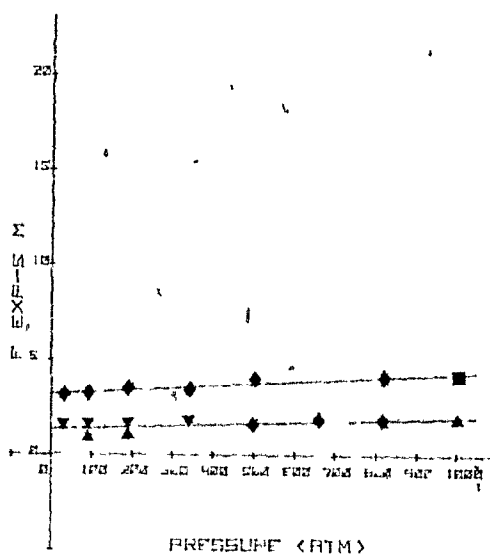
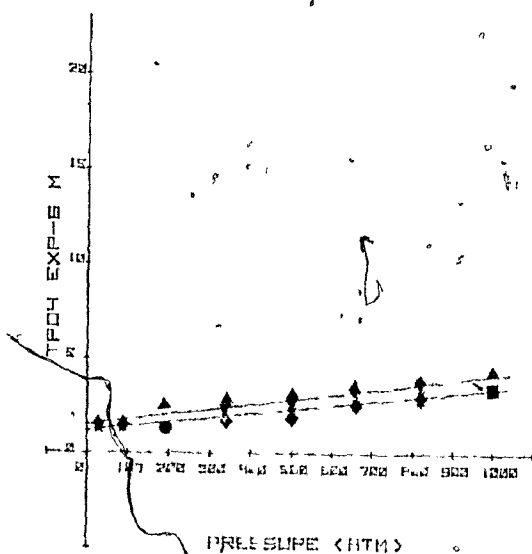
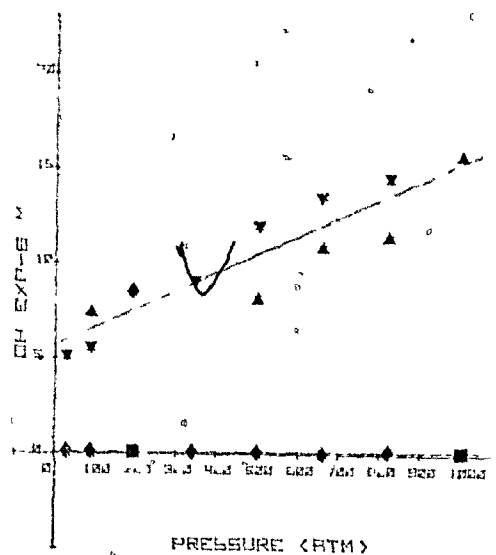
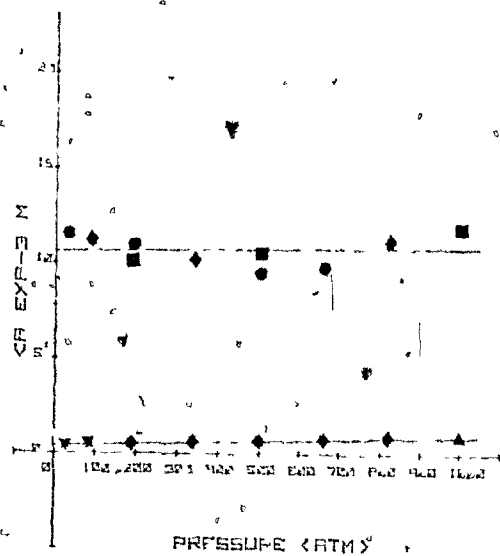
decreasing pressure

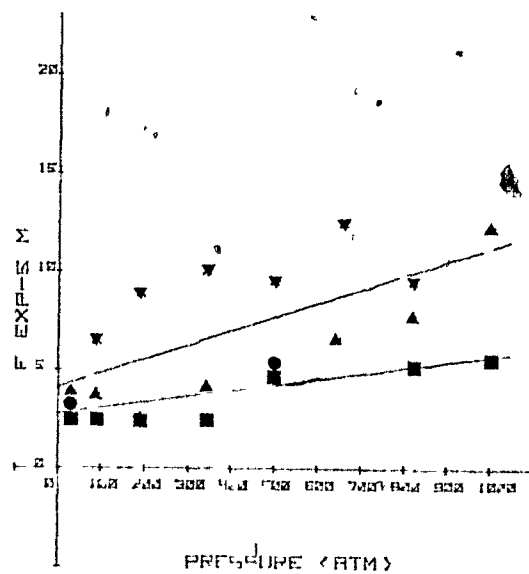
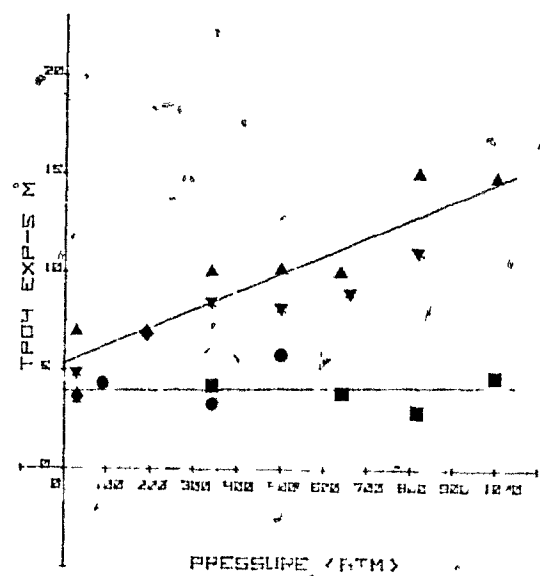
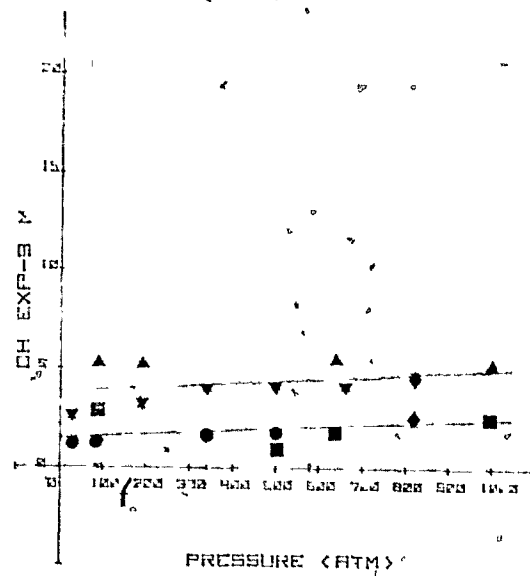
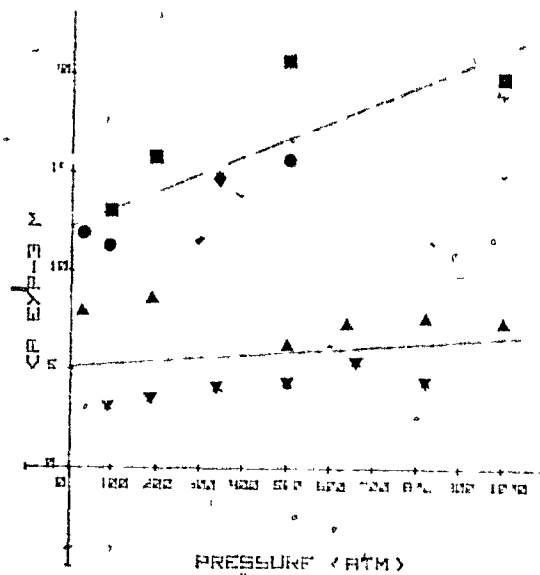
◆ : seawater

◆ : 0.65N NaCl Solution

common points







Effect of Temperature on the Dissolution of
Apatite in 0.65N NaCl Solution (1 atm.)

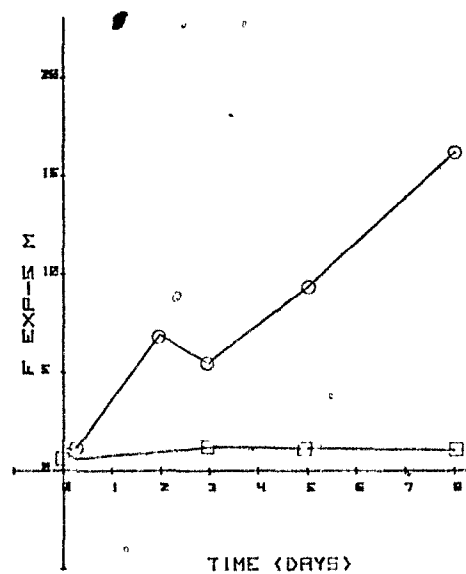
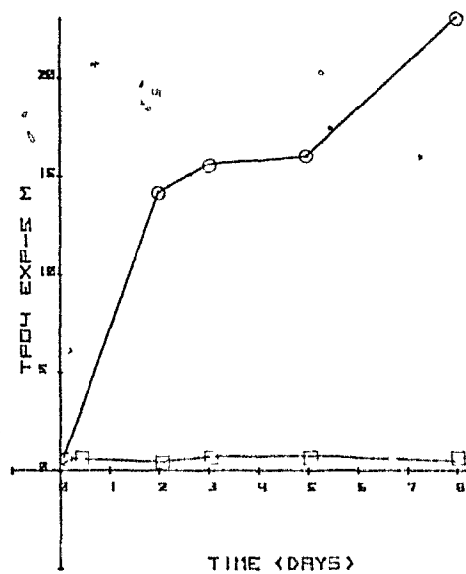
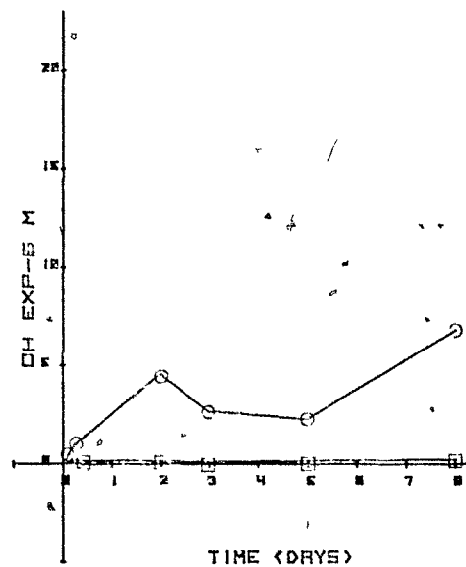
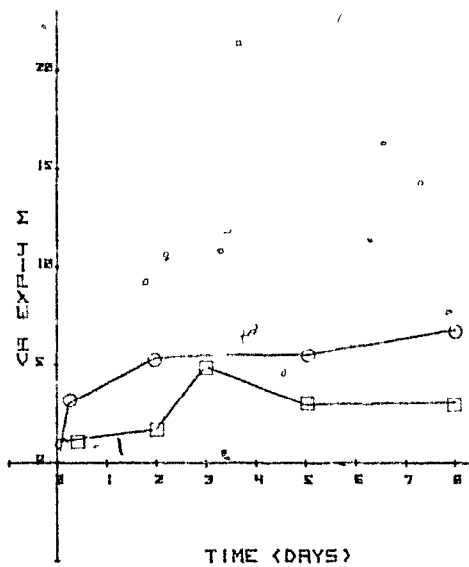
Figure R36: Ontario

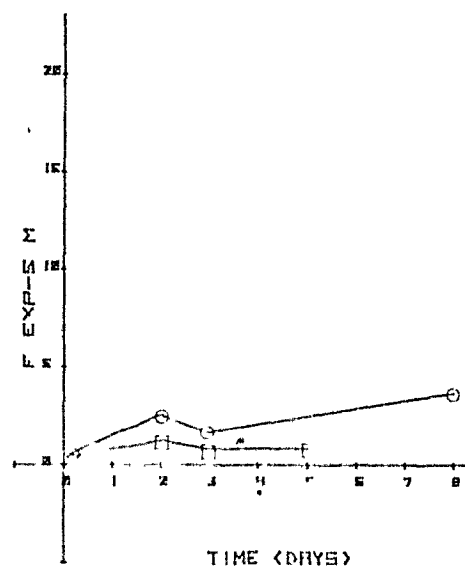
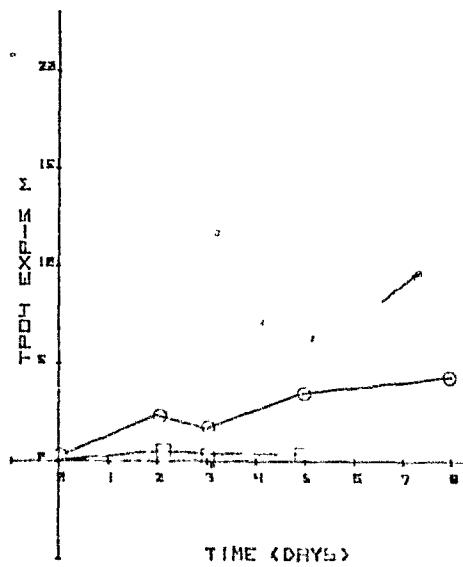
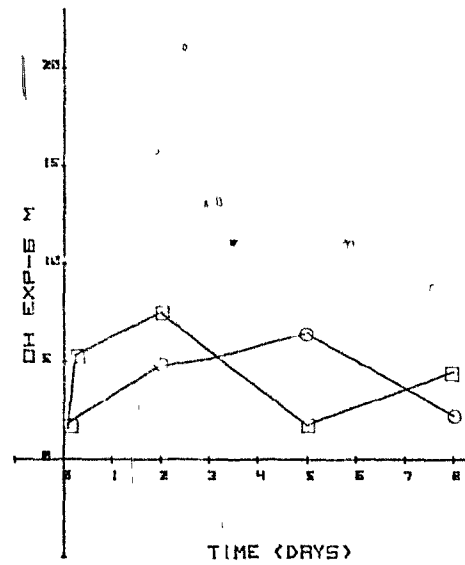
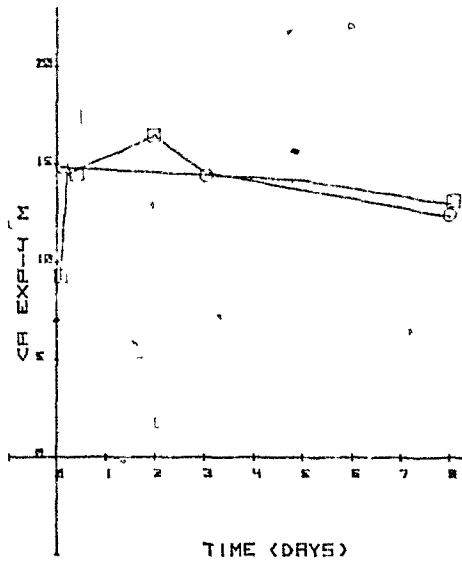
R37: Quebec

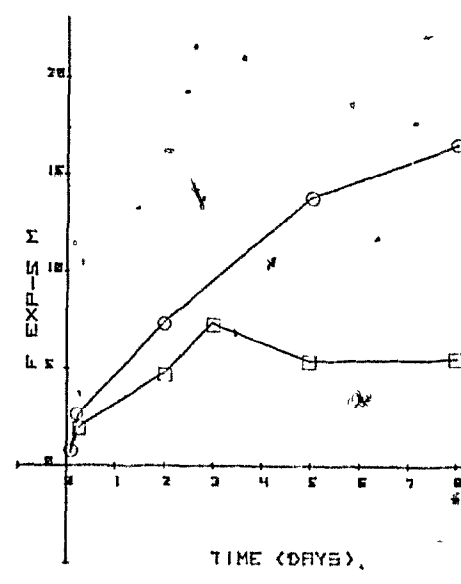
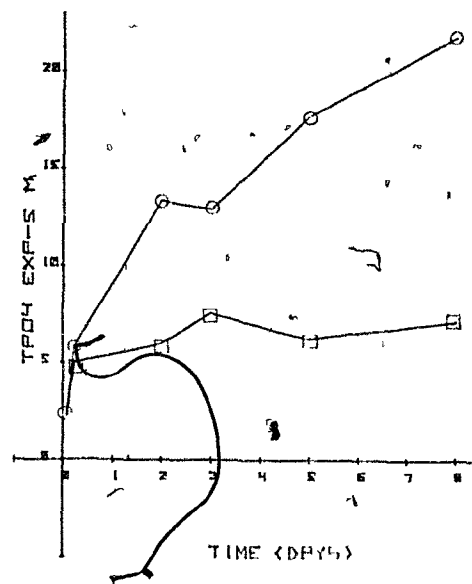
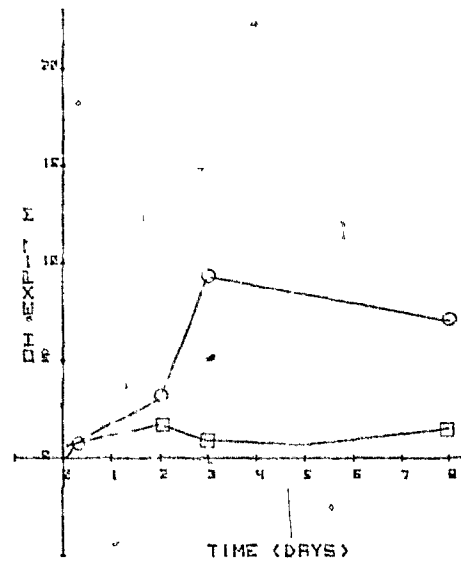
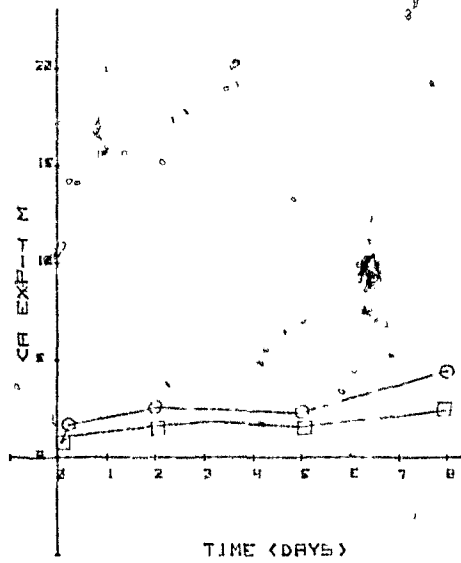
R38: Mexican

○: 2°C

□: 25°C







days, 1 atm.), The graphs of concentration variation versus time are given in Figures R39-R42. The small differences in solubilities over the fairly large temperature range are similar to the small differences in Kramer's data (1964).

B.III: Reaction with NaCl Solutions at High Pressures

To test the combined effects of temperature and pressure, the solubility of Mexican apatite in NaCl solution at 5° and 14°C over the pressure range 30-1000 atm. was measured. The results for total phosphate are given in Figure R43. Unfortunately, the experiment had to be terminated for other reasons as the pressure was being decreased in the 14°C run. However, the two temperature curves do show a significant difference. In each temperature case a good least-squares linear correlation of total phosphate variation with pressure variation was obtained as pressure was both increased and decreased. The experiment shows that although a general increase in solubility with increasing pressure can be predicted, other effects can alter this pattern. From the results presented here, the effect of an NaCl solution of 5°C, 100 atmospheres is approximately equivalent to an NaCl solution of 14°C, 500 atmospheres.

C. Common Ion Effects in NaCl Solutions

CF. Spiked NaCl Solutions

In an effort to separate the combined effects of common

Effect of Temperature on the Dissolution of
Apatite in Seawater (1 atm.)

Figure R39: Ontario

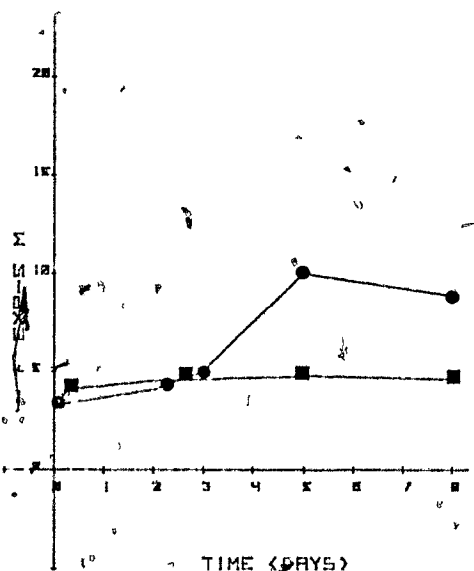
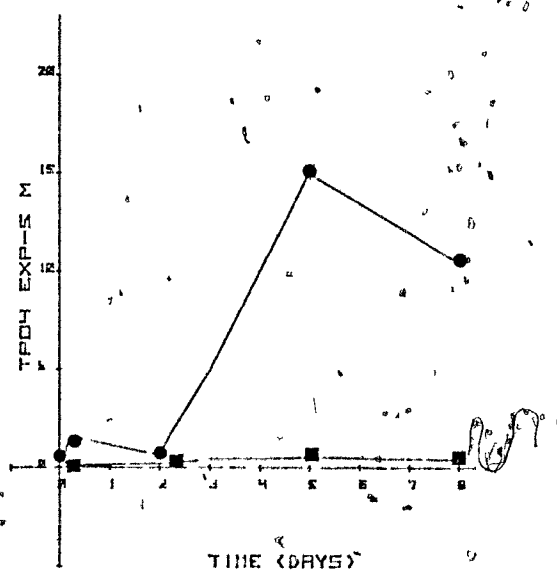
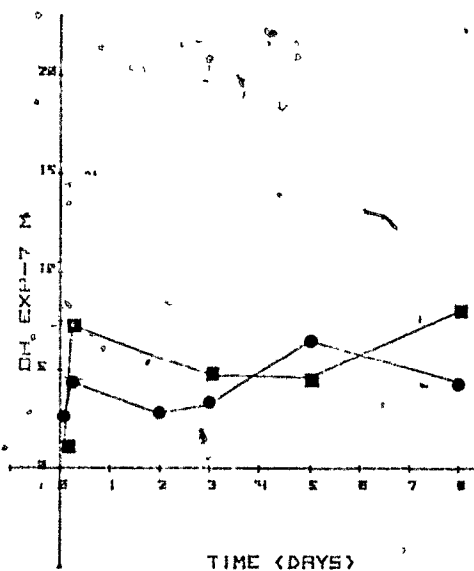
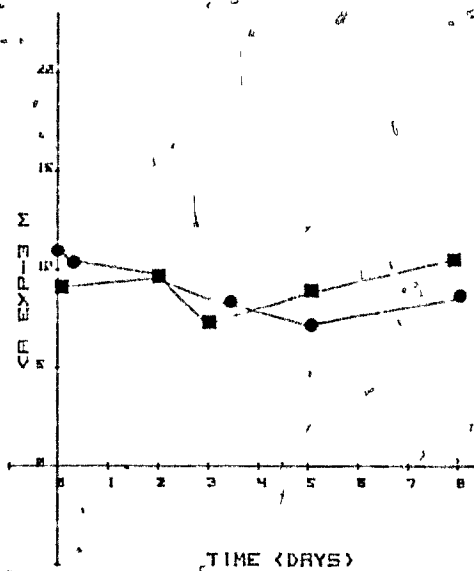
R40: Quebec

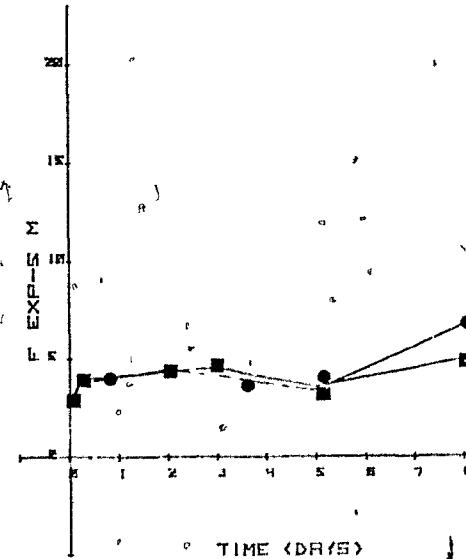
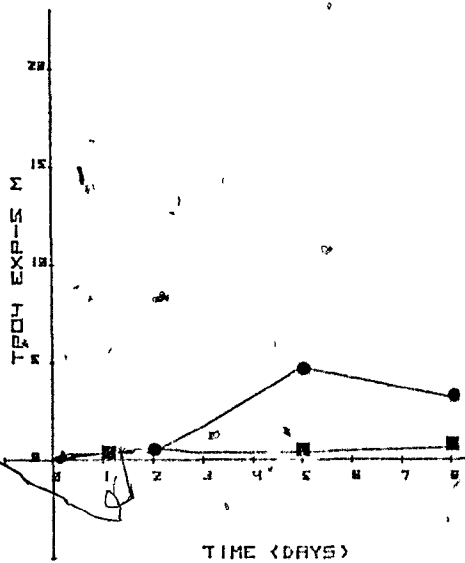
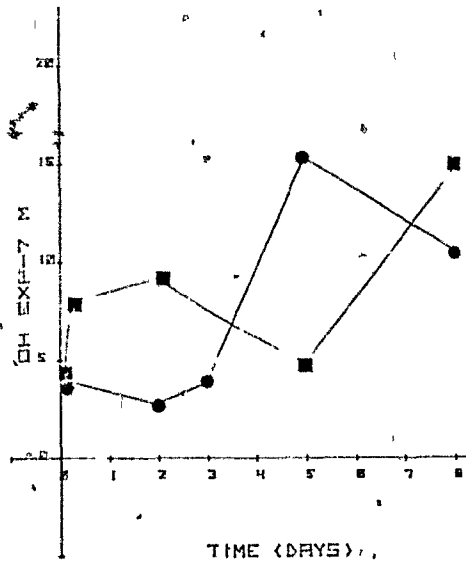
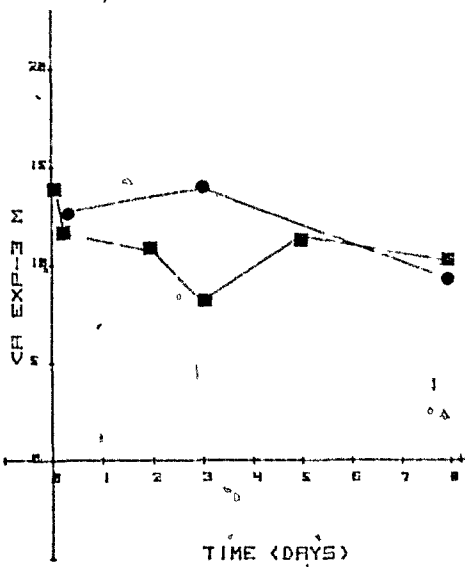
R41: Mexican

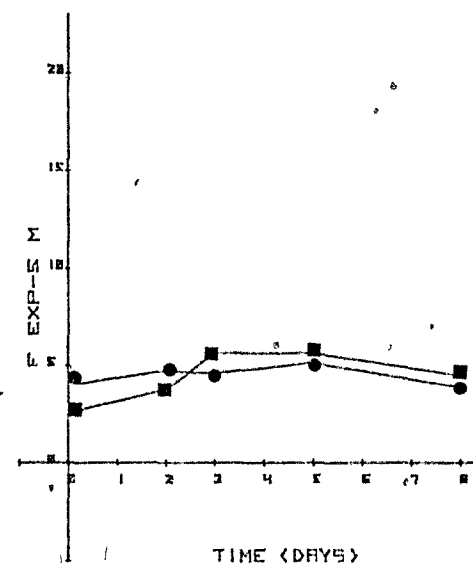
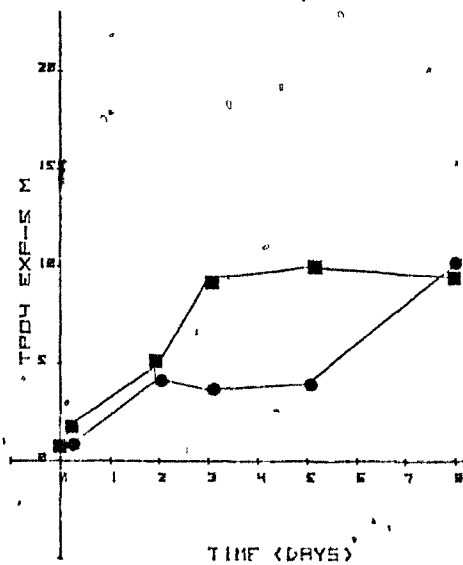
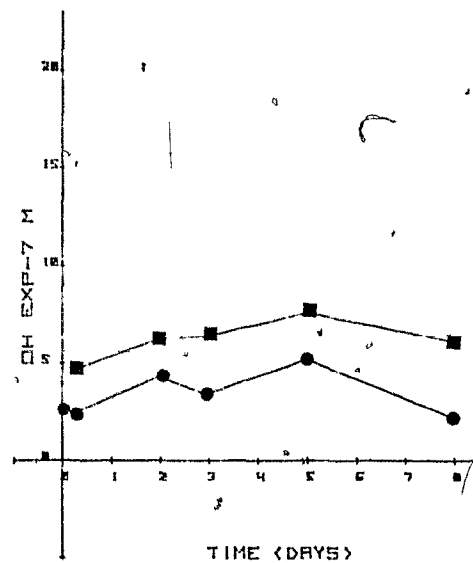
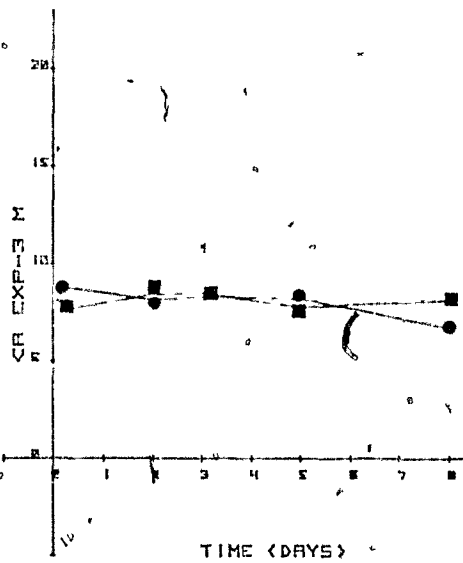
R42: Florida Collophane

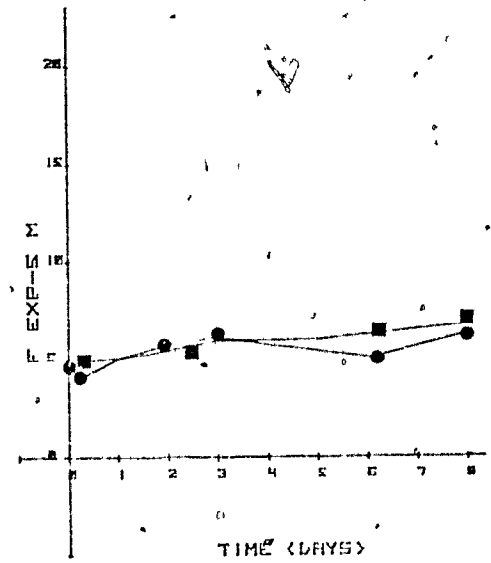
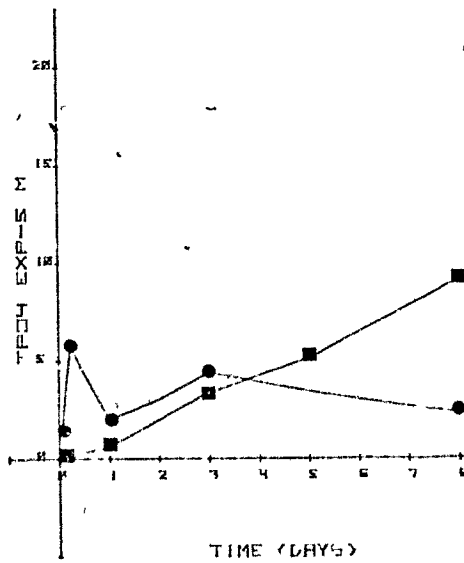
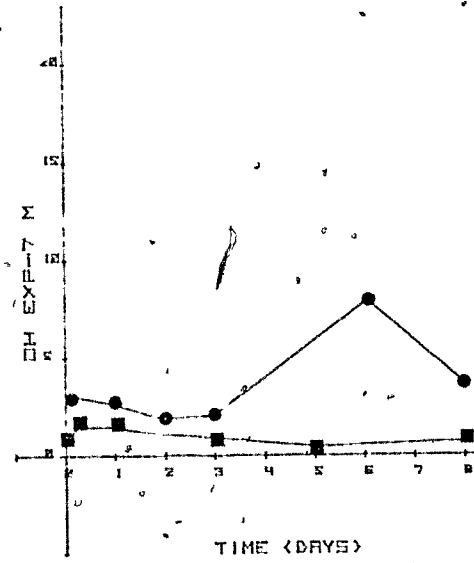
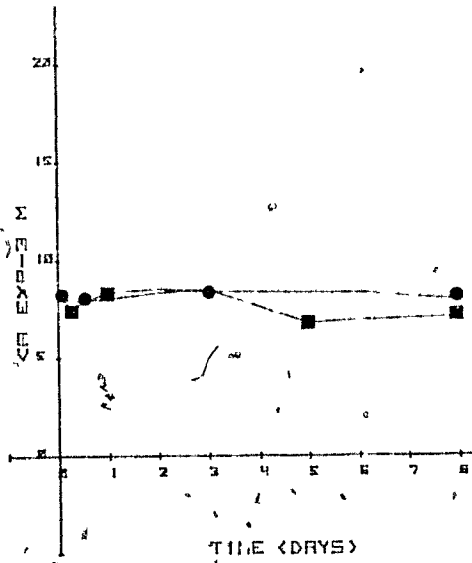
● : 2°C

■ : 25°C









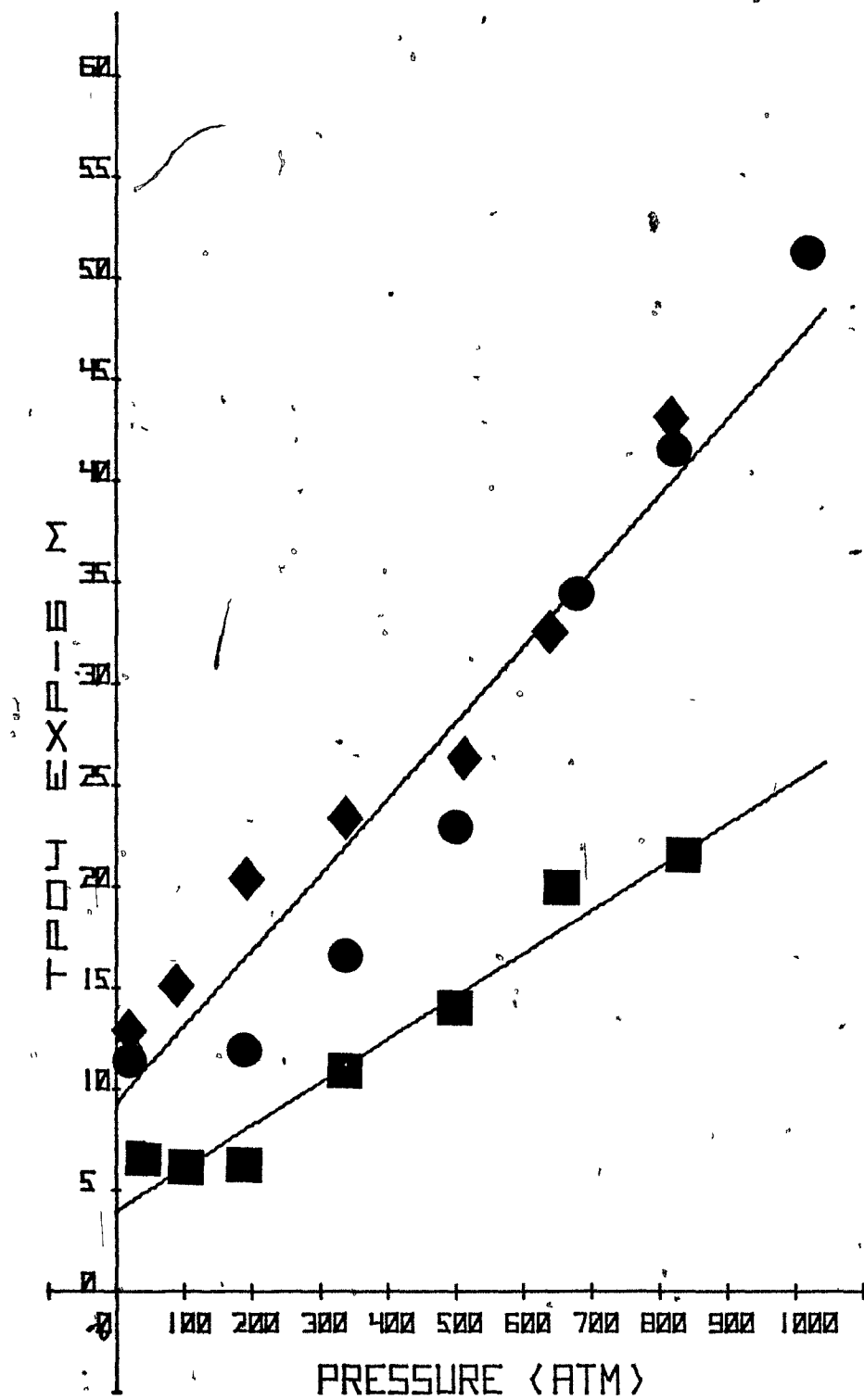
Comparison of the Effect of Temperature
combined with the Effect of Pressure on the
Dissolution of Mexican Apatite in 0.65N NaCl
Solution

Figure R43

- ◆ : decreasing pressure
 - : increasing pressure
 - : 14°C (increasing pressure only)
- 5-6°C

Line is least-squares linear regression





ions found in seawater, apatite solubilities were tested in NaCl solutions (1 atm., 2°C, 8 days) containing concentrations of various common ions: calcium (10^{-4} M and 10^{-2} M), phosphate (50 micromolar) and fluoride (5 and 1000 ppm).

The common ion spikes were chosen to be reasonably representative of upwelling zone pore water conditions. Sholkovitz (1973) has reported a decrease in calcium with depth in the sediments of anoxic basins. Both he and Burnett (1974) have reported an increase of phosphate with depth from the normal seawater concentration of about 2 micromolar to above 50 micromolar within 15 cm of sediment. Shiskina et al. (1973) have reported interstitial fluoride concentrations of 11 ppm in Peruvian upwelling zone sediments. The very high level of 1000 ppm NaF was chosen to induce substantial reaction within relatively short periods of time.

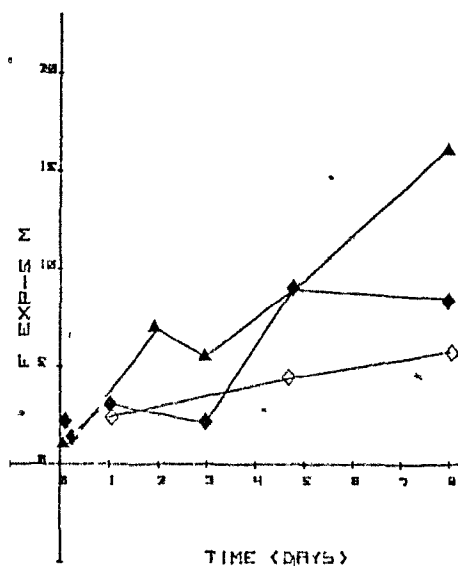
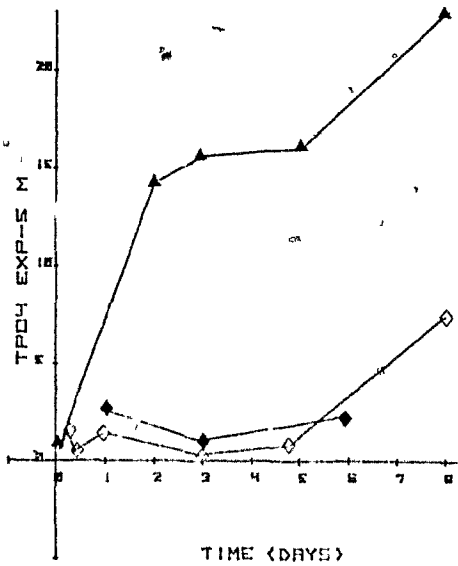
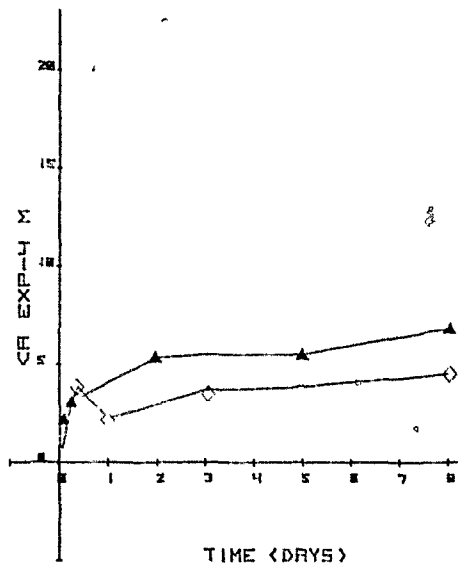
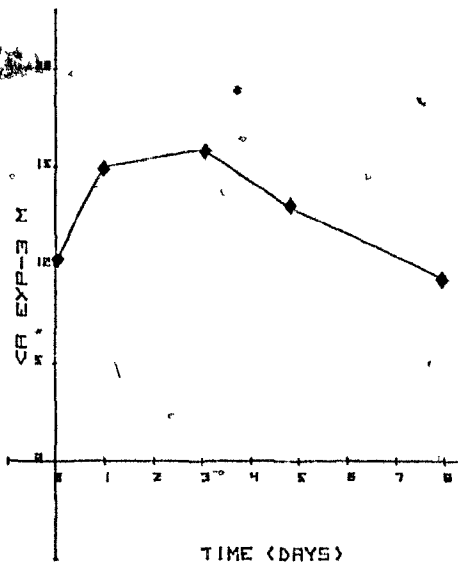
Addition of 50 micromolar phosphate (Figures R44 & R46) depressed the solubility of Ontario apatite in terms of total phosphate and to a lesser extent in terms of calcium. This is similar to the effect seen by Dedhiya et al. (1973, 1974), who noted a decrease in solubility of hydroxyapatite in 0.5 N NaCl, pH 4-5 solutions when 10^{-3} M phosphate spikes were used.

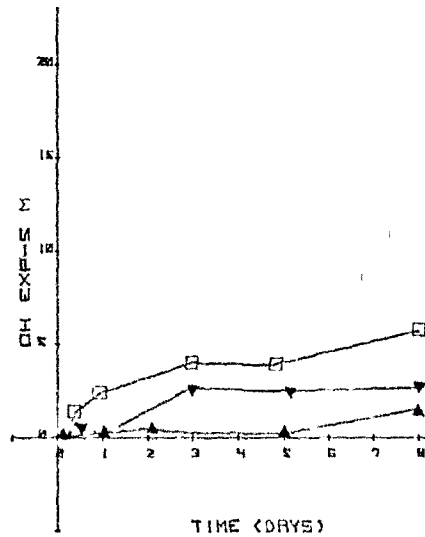
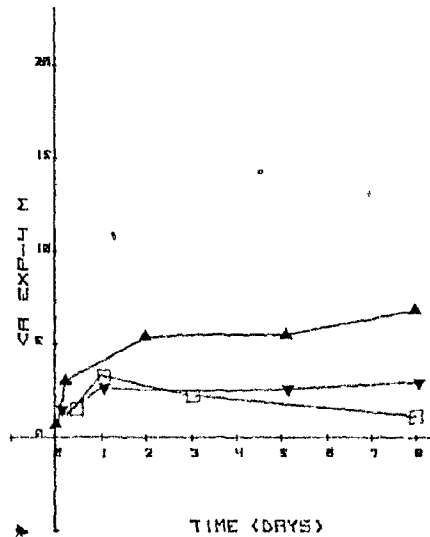
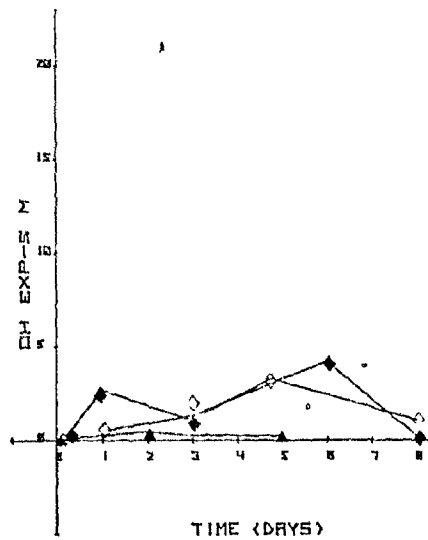
Addition of 5 ppm NaF (Figures R47 and R48) caused a decrease in both total phosphate and calcium levels for the Quebec and Ontario apatites. The fluoride concentration in the spiked solution for the Ontario apatite remained relative-

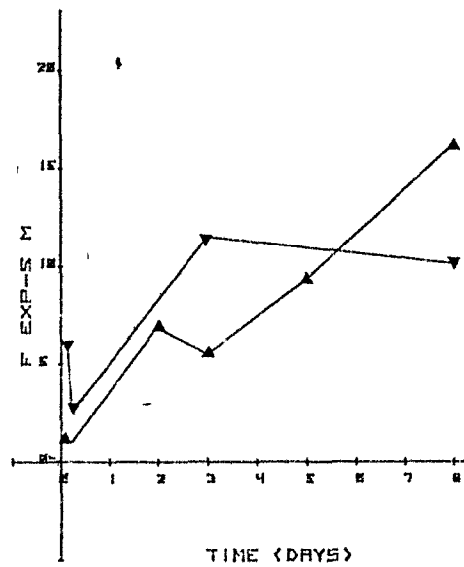
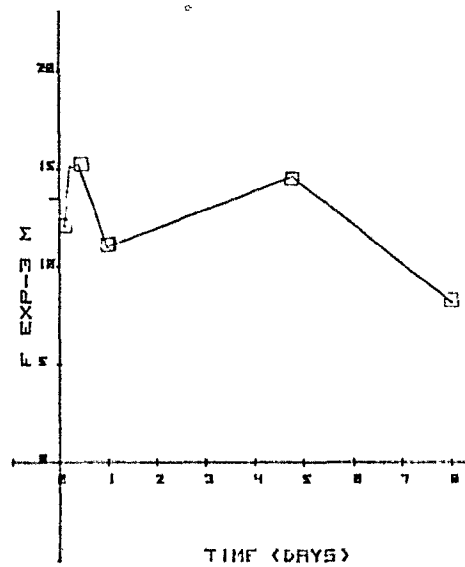
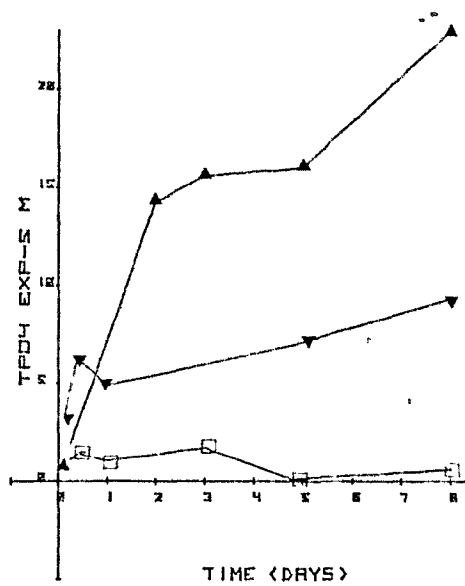
Effect of the Addition of Common Ions on the
Dissolution of Ontario Apatite in 0.65N NaCl
Colution (2°C , 1 atm.)

Figures R44 - R46

- ▲: unspiked 0.65N NaCl Solution
- ◇: spiked to 10^{-4}M Ca
- ◆: spiked to 10^{-2}M Ca
- ▼: spiked to $5 \times 10^{-5}\text{M}$ phosphate
- : spiked to 1000 ppm NaF







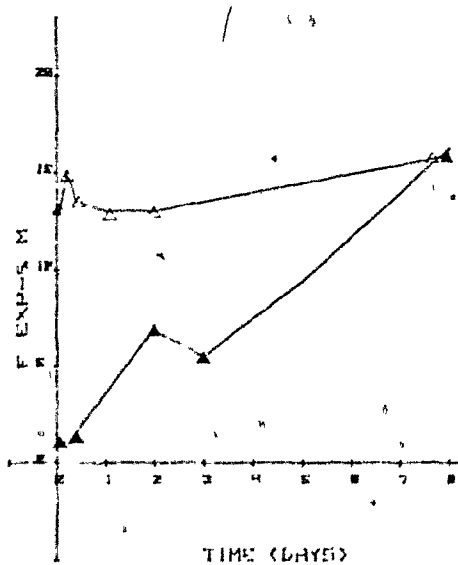
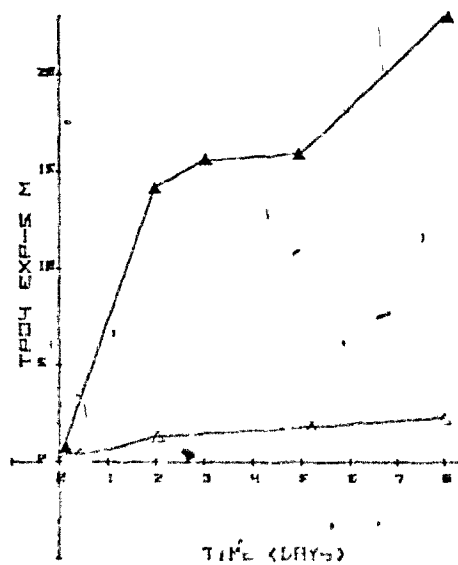
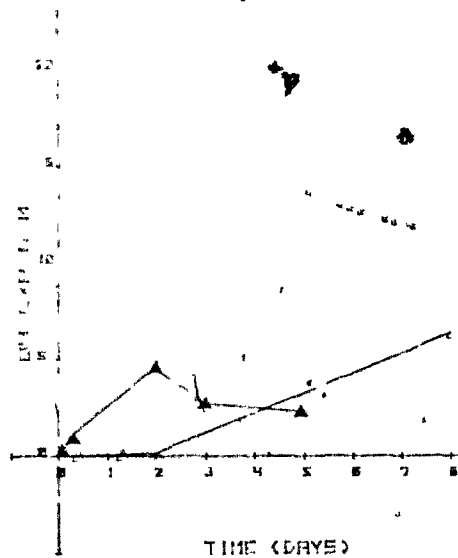
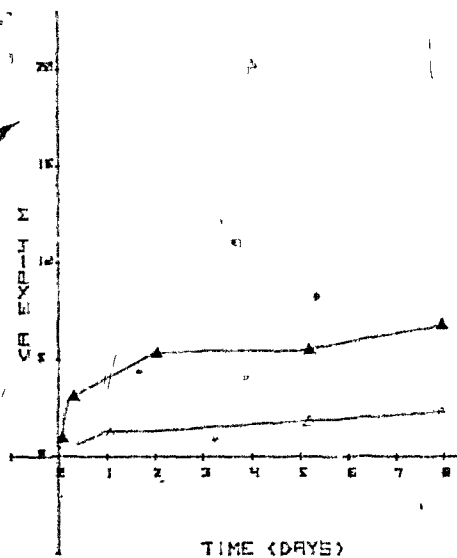
Effect of Addition of 5ppm NaF to the
Dissolution of Apatite in 0.65N NaCl
Solution (1 atm., 2°C)

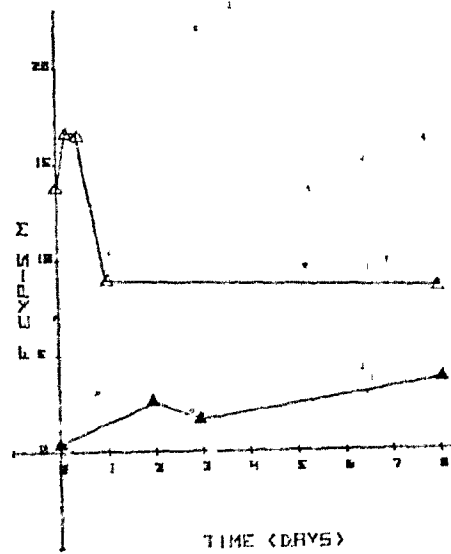
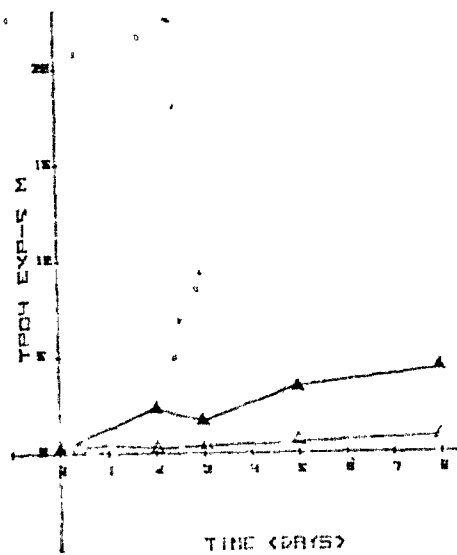
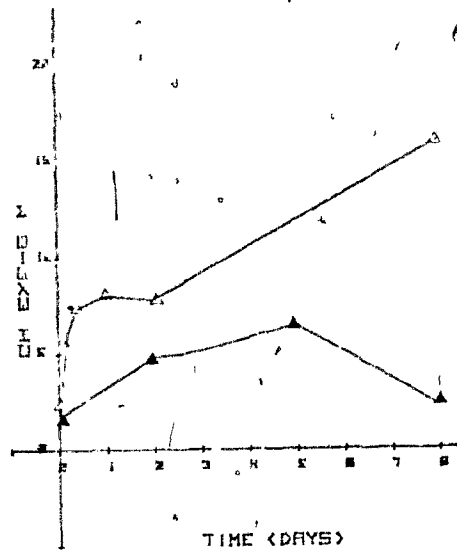
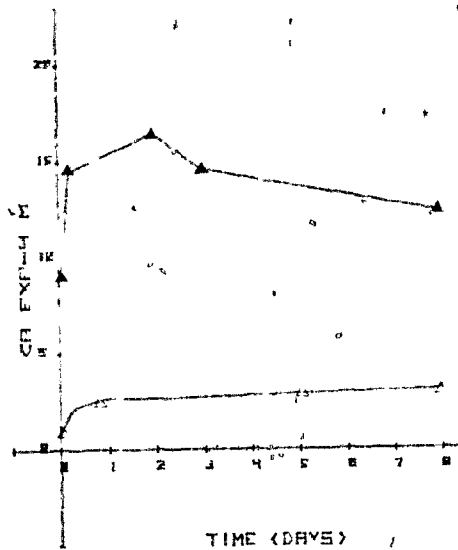
Figure R47: Quebec

R48: Ontario

▲ : unspiked 0.65N NaCl Solution

△ : spiked to 5ppm NaF





ly stable, while the level in the regular NaCl solution increased, indicating an input of ion into the solution. On the other hand, for the Quebec apatite there was no uptake of fluoride, and to a lesser extent calcium from the spiked solution, while the fluoride level in the unspiked solution remained fairly constant. These decreases might indicate the precipitation of a CaF_2 phase, since the solubility product is approximately equaled in the Quebec case after about one day. For both apatites, a stable rate of dissolution in fluoride was achieved after about eight days, as the fluoride level in the spiked and unspiked solutions was about equal at that time. The difference in the fluoride behavior of the two apatites can be explained in terms of their bulk fluoride content (Appendix A, Table A1).

The 10^{-4} and 10^{-2} M calcium spiked solutions (Figures R45/46) both caused significant decreases in total phosphate for the Ontario apatite, but fluoride was only slightly decreased. The calcium variation for the 10^{-4} solution was about the same as for the unspiked solution, whereas the 10^{-2} solution showed a decrease in calcium with time. The decrease in phosphate and calcium indicates the precipitation of a calcium phosphate, but high levels of calcium are necessary before this precipitation could take place.

The NaCl solution spiked to 1000 ppm fluoride significantly reduced the solubility of Ontario apatite (Figures R44/45) in terms of total phosphate and calcium. There was

a decrease with time in terms of fluoride and to a lesser extent calcium. This uptake of fluoride by the Ontario apatite is interesting in light of the performance seen in the 5 ppm NaF solution (Figure R48). Obviously a new fluoride-containing phase is precipitating out rapidly and this new phase is interfering with the dissolution process, as represented by the total phosphate concentration.

C.II. Comparison of Solubilities in NaCl and Seawater Solutions

Figures R49-R51) show comparisons of solubilities of Mexican, Ontario, and Quebec apatites in NaCl and seawater solutions (1 atm. and 2°C).

In the case of the Mexican apatite, solubility was significantly less in seawater than in NaCl solution. The high background concentration of calcium in seawater tended to mask any changes in the solubility.

A similar behavior in terms of total phosphate and calcium concentrations was noted for the Ontario apatite. The exception here is the fluoride concentration. The variation of fluoride with time for both NaCl and seawater solutions was similar and comparison to the result obtained with the NaCl + 5 ppm NaF indicated that in both the NaCl and seawater solutions the high fluoride concentration in solution was the stable rate (in terms of rate of dissolution) case. This is reasonable in terms of the high fluoride content of the bulk solid.

Comparison of the Effect of Dissolution of
Apatite in Seawater to Dissolution in 0.65N NaCl
Solution (1 atm., 2°C)

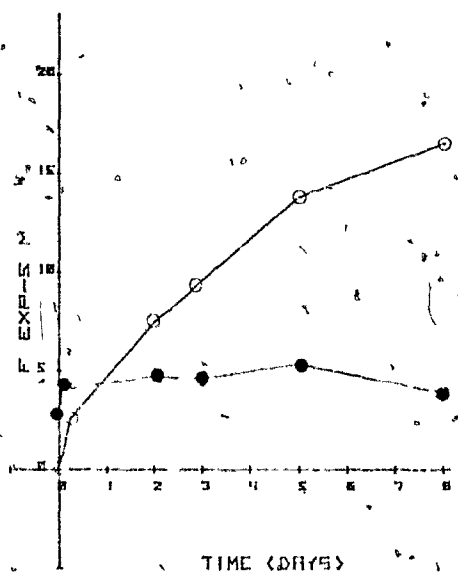
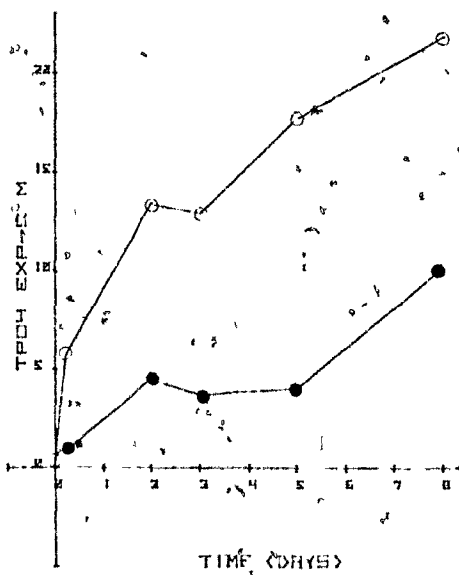
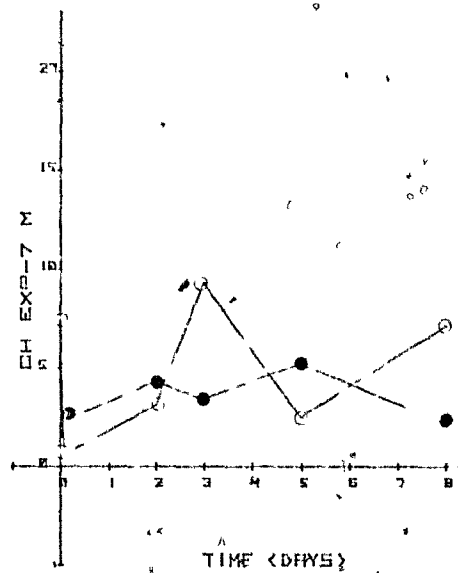
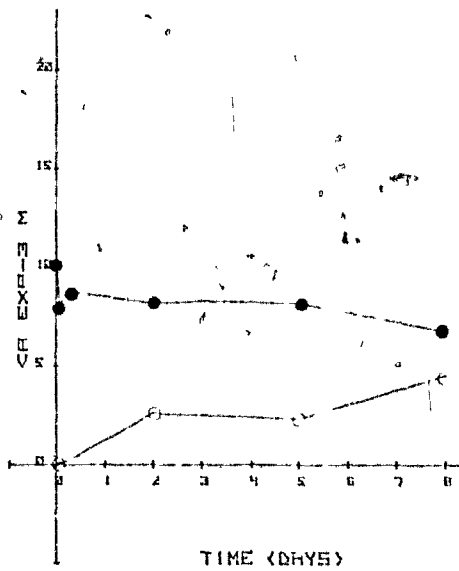
Figure R49: Mexican

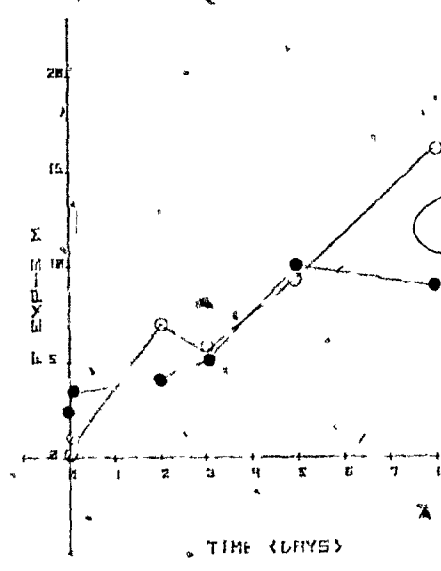
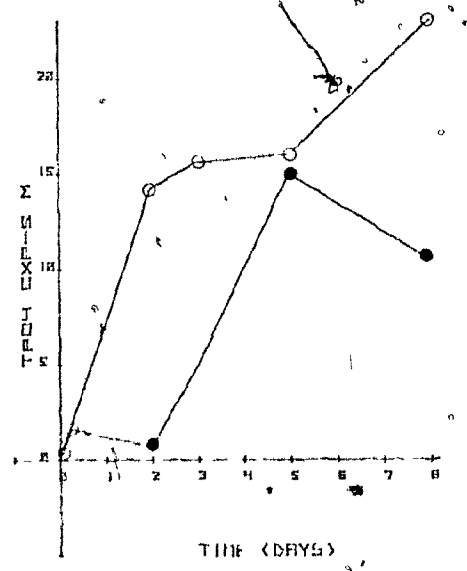
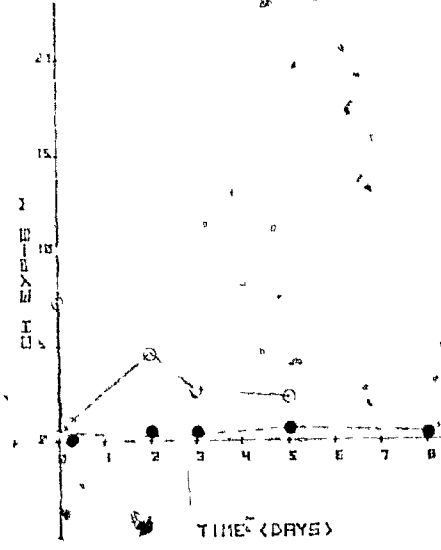
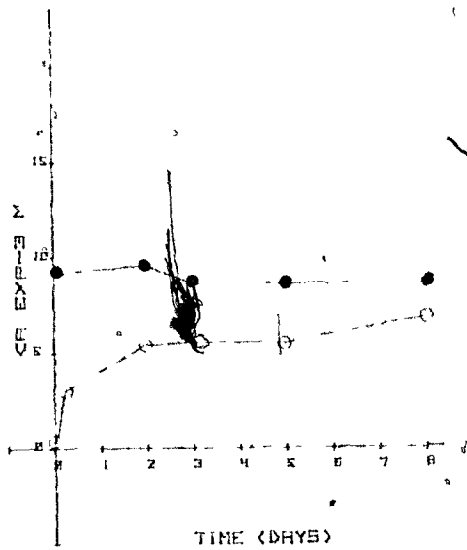
R50: Ontario

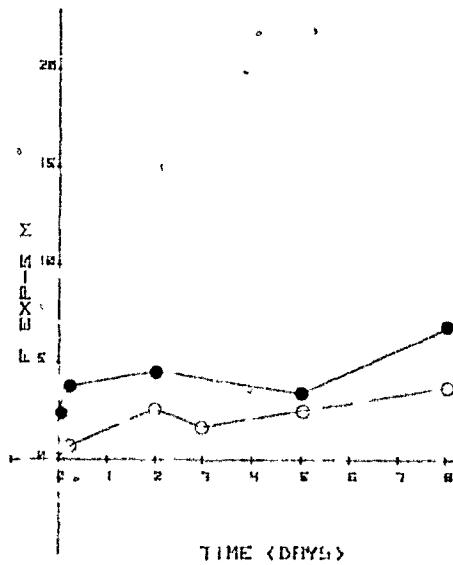
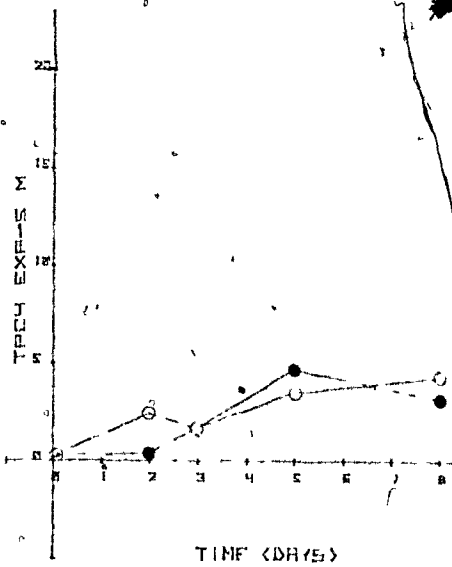
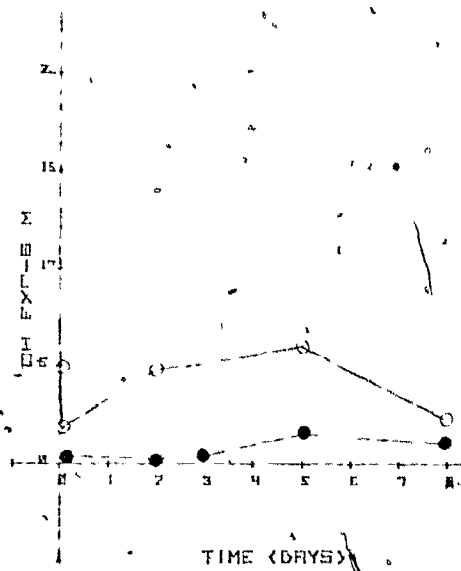
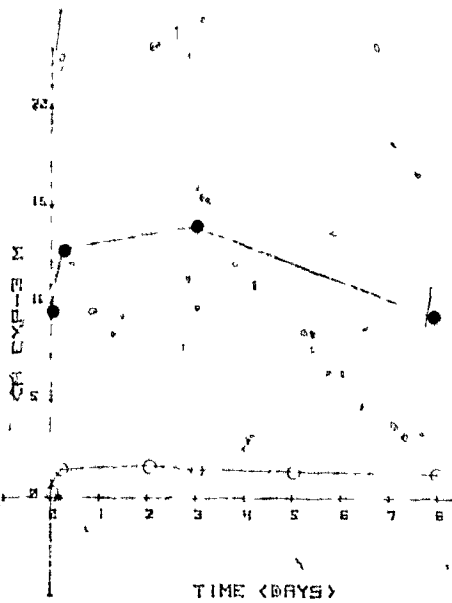
R51: Quebec

○ : 0.65N NaCl Solution

● : Seawater







In the case of the Quebec apatite, the solubility in both the NaCl and seawater solutions was very similar. This indicates that the alteration of the original surface phase on the apatite, due to exposure to seawater, must take a fair length of time (i.e., greater than eight days). The two other apatites formed altered surfaces much faster, when exposed to seawater, but the composition of the newly-formed surface was strongly dependent on the original composition of the apatite.

D. Reaction With Spiked Seawater

D.I. Phosphate-Spike

Dedhiya et al. (1973, 1974) have found that phosphate concentrations in excess of $10^{-3}M$ decrease both the rate and the degree of dissolution of hydroxyapatite in 0.5 N NaCl solutions. In these experiments, (Figures R52, R53) phosphate levels that could be expected in anoxic pore waters, similar to pore water concentrations of the Peruvian upwelling zone (Burnett, 1974) were used. These were several times phosphate levels found in seawater. Both the Mexican and Florida apatites showed no change from the behavior for unspiked seawater at 1 atm. and $2^{\circ}C$. Since the initial phosphate levels are about two orders of magnitude below that of Dedhiya et al. (1973, 1974), little effect on the solubility was expected.

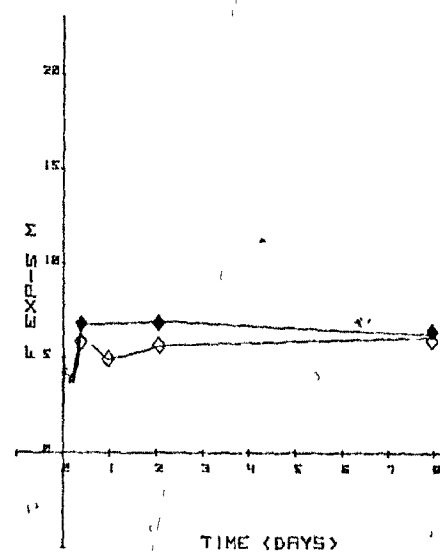
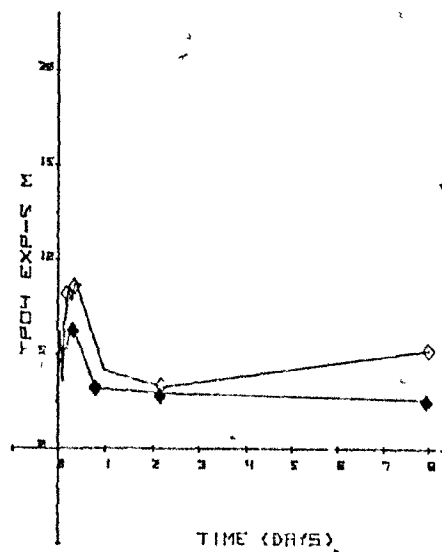
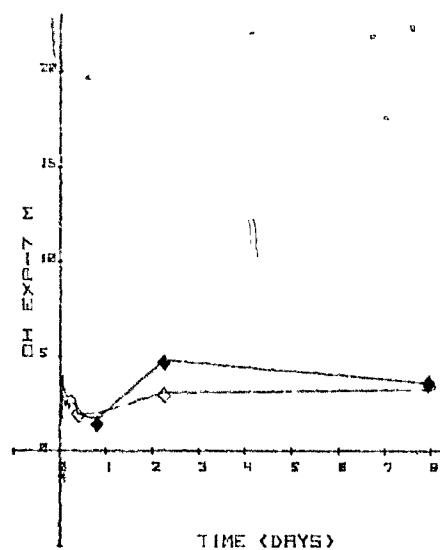
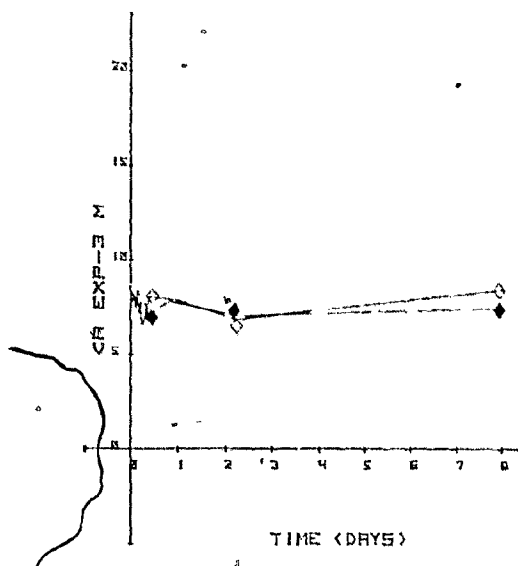
At pH 8 in seawater about 90% of the total phosphate exists as $(HPO_4^{=})$ and about 9% as (PO_4^{-3}) . Only about 30% of

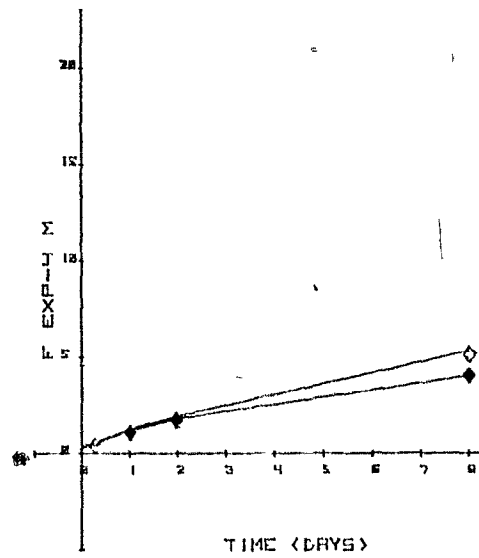
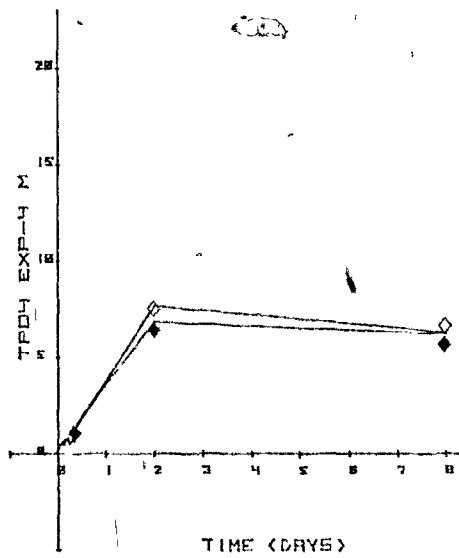
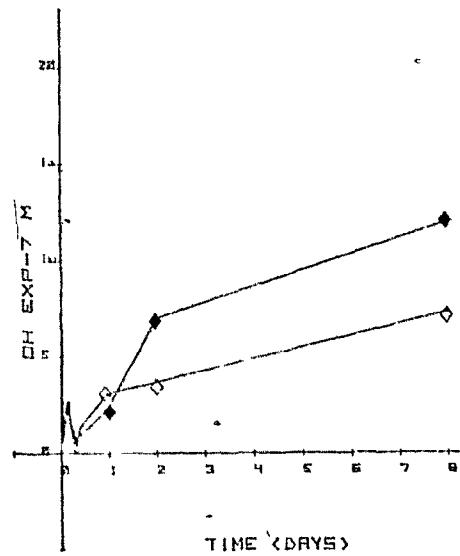
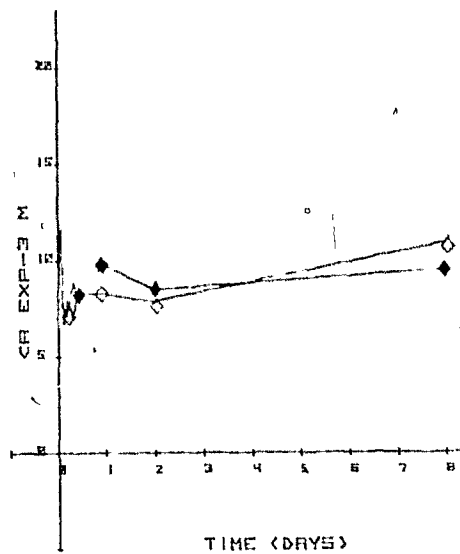
Comparison of the Effect of Phosphate
Spikes on the Dissolution of Apatite in
Seawater

Figure R52: Florida

R53: Mexican

- ◆ : seawater spiked to 2.5×10^{-5} M phosphate
- ◇ : seawater spiked to 5×10^{-5} M phosphate





the $(\text{HPO}_4^=)$ exists free in solution, the remainder being ion-paired, and only 0.01% of the (PO_4^{-3}) is free, the rest being ion-paired (Atlas, 1975). These values indicate that the phosphate spike was essentially neutralized by ion-pairing in seawater. Therefore, in order to decrease the solubility of apatites, much higher phosphate concentrations than even those found in anoxic pore waters of upwelling zones is needed.

D.II. Low-Fluoride Spike

The solubility of Florida apatite (Figure R54) in seawater spiked with 0.35 and 3.5 ppm NaF was determined. There was essentially no difference between the behavior of the apatite in the two spiked solutions and that found in unspiked seawater. McCann (1968) has noted that solutions high in pH and with low fluoride content do not exceed the solubility product of CaF_2 . The fluoride level in the more concentrated spiked solution remained essentially level.

D.III. High Fluoride Spike

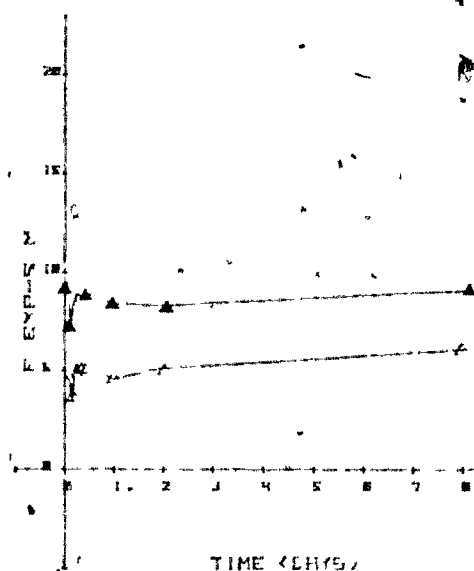
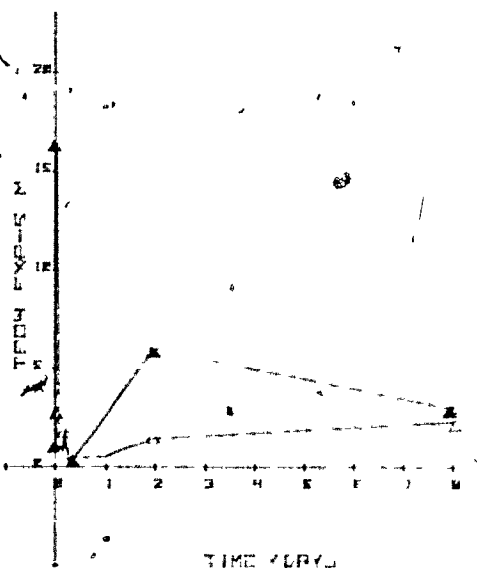
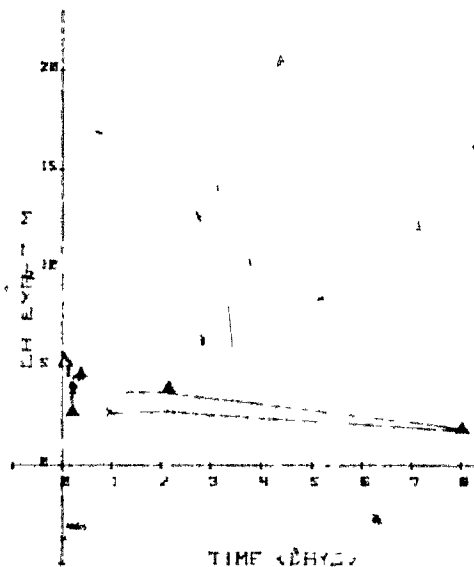
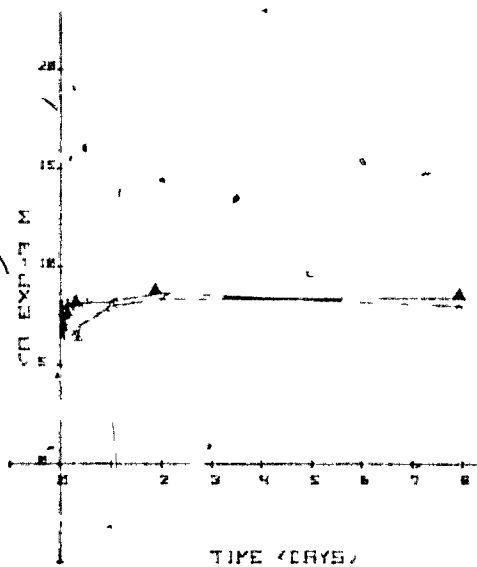
The solubilities of the Mexican (Figure R55) and Ontario (Figure R56) apatites in seawater spiked to 100 to 500 ppm NaF (1 atm., 2°C) and those of Florida (Figure R57) and Marine (Figure R58) in 500 ppm NaF spiked seawater were determined. These fluoride levels are very high in comparison

Comparison of the Effects of Low Level
Spikes of Fluoride on the Dissolution of
Florida Apatite in Seawater (1 atm., 2°C)

Figure R54

△ : spiked to 0.35 ppm NaF

▲ : spiked to 3.5 ppm NaF



Comparison of the Effect of High Levels of
Fluoride Spikes on the Dissolution of
Apatite in Seawater (1 atm., 2°C)

Figure R55: Mexican

R56: Ontario

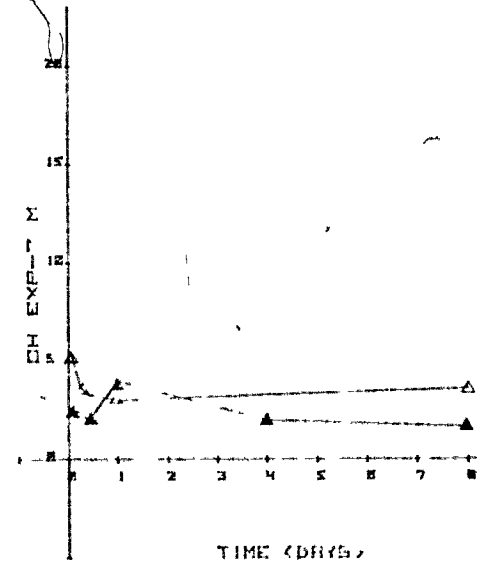
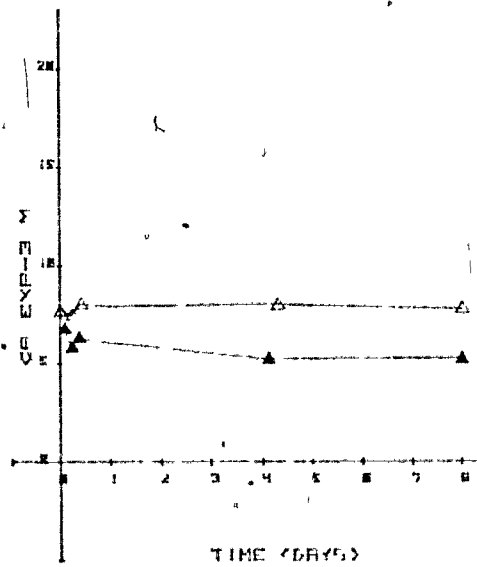
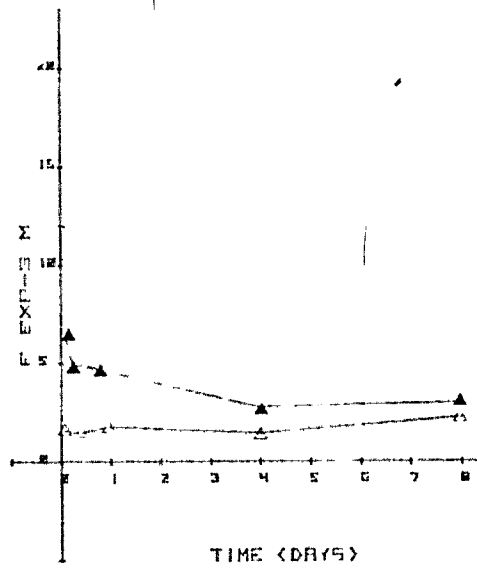
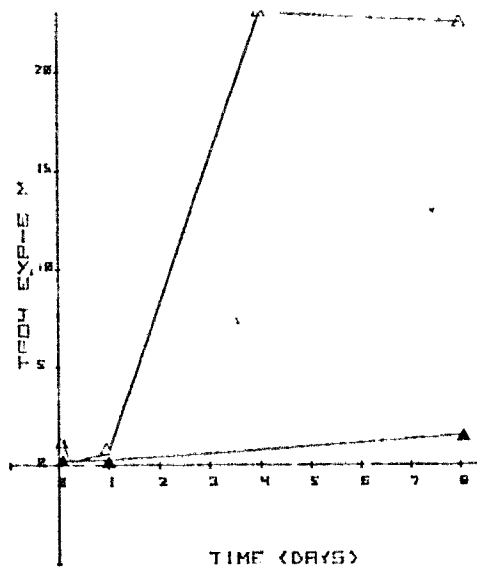
R57: Florida

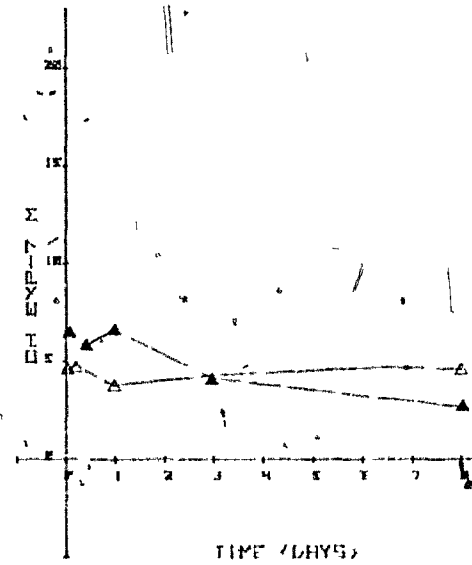
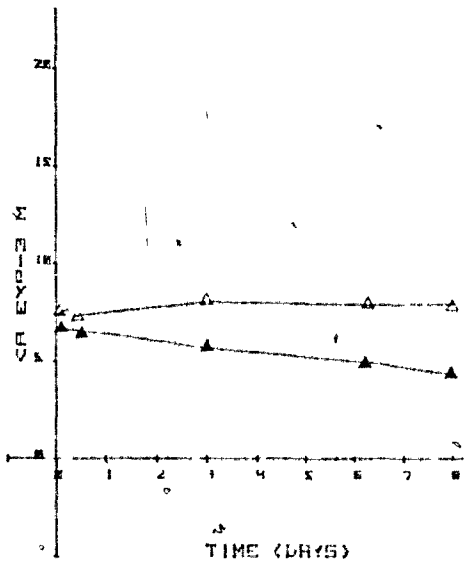
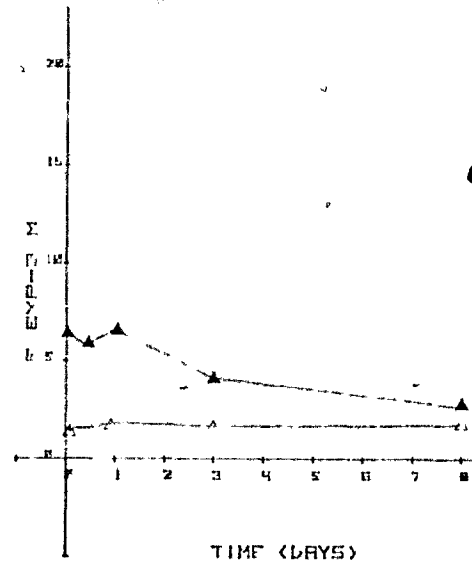
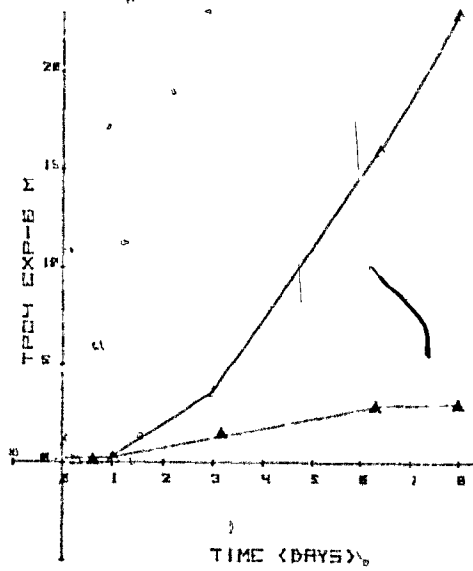
R58: Marine

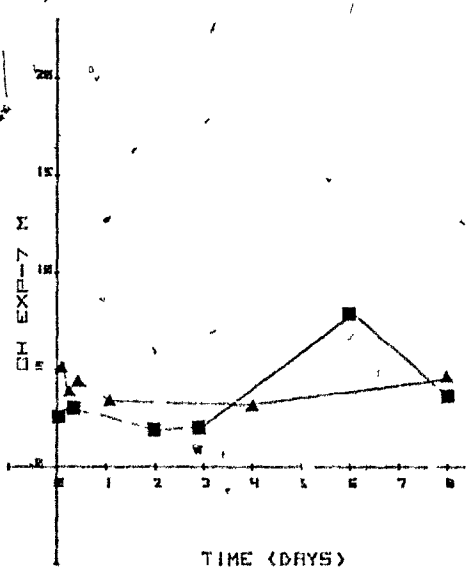
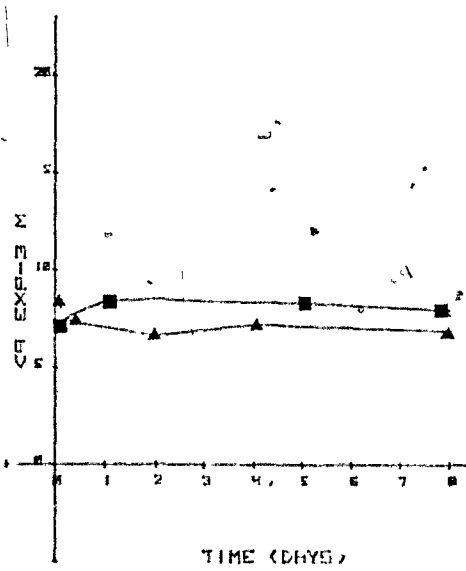
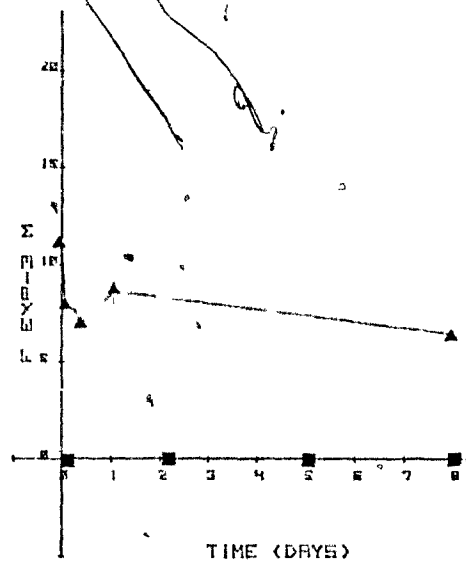
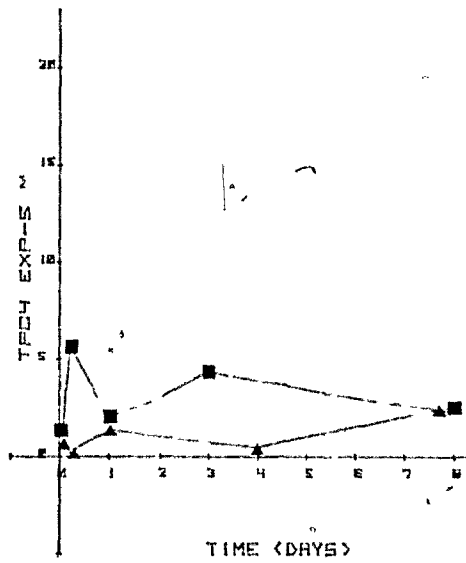
■ : unspiked seawater

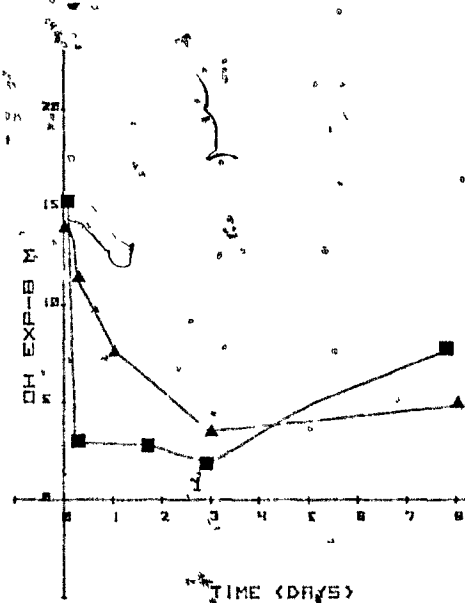
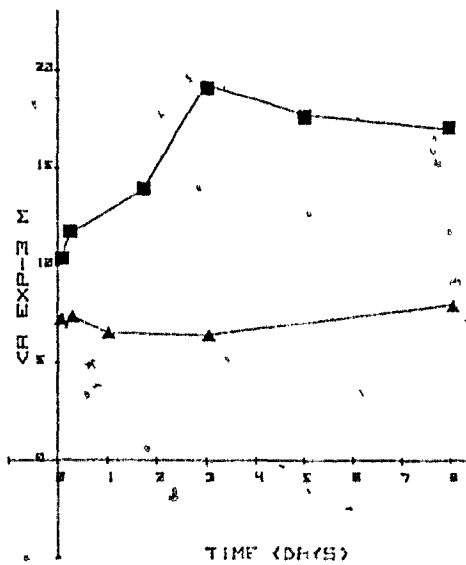
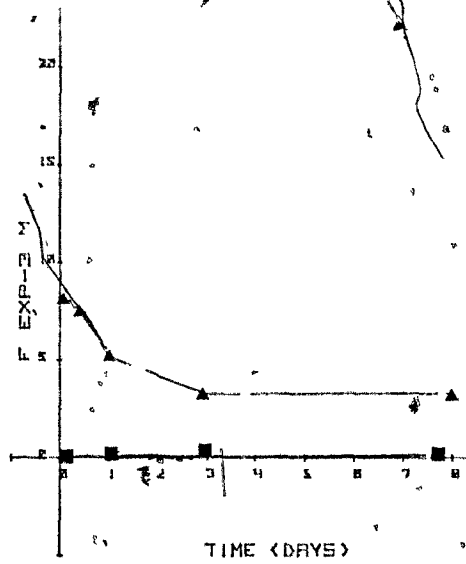
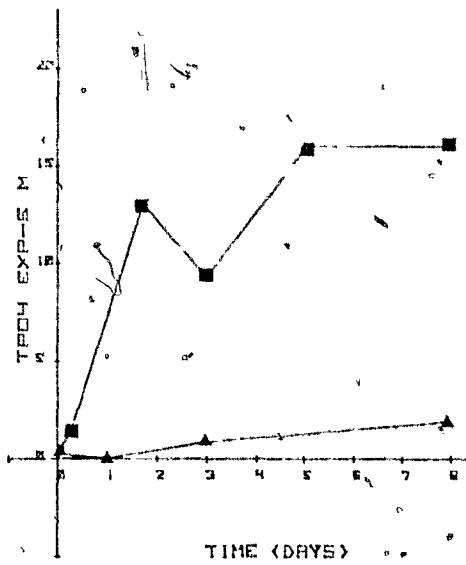
△ : spiked to 100 ppm NaF

▲ : spiked to 500 ppm NaF









to normal seawater levels (~ 2 ppm) or even to interstitial Peruvian upwelling pore waters of ~ 12 ppm (Shiskina et al., 1972), but they are reasonable in light of the report of Simpson (1969) who found that fluoride levels of $10^2 - 10^3$ times normal seawater were necessary to precipitate, in laboratory experiments, a solid phase identifiable as fluorapatite.

In each of the 500 ppm experiments, there was a decrease in fluoride coupled with a slight decrease in calcium. The total phosphate was significantly reduced. If we take the total phosphate concentration to represent the solubility of the apatite, then the addition of the 500 ppm NaF spike caused a significant decrease in apatite solubility. McCann (1968) found that CaF_2 would precipitate from solution at pH 7.2 when the fluoride level was 5 ppm, however, low levels of phosphate lowered the maximum pH level possible for CaF_2 precipitation from a 5 ppm solution. This decrease in the maximum possible pH because of phosphate interference may be the cause of the essentially level fluoride variation for the 100 ppm solutions. Farr and Elmore (1962) found in their study that in some cases supersaturation of CaF_2 was possible and that this meta-stable situation lasted for longer than a year.

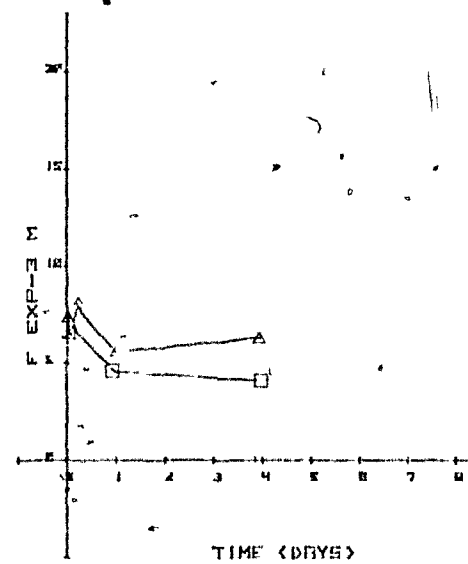
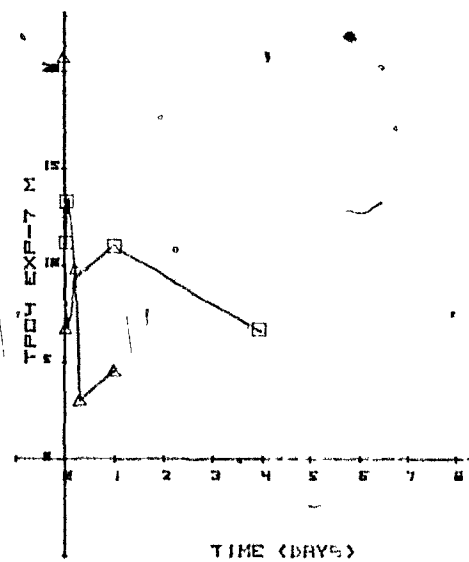
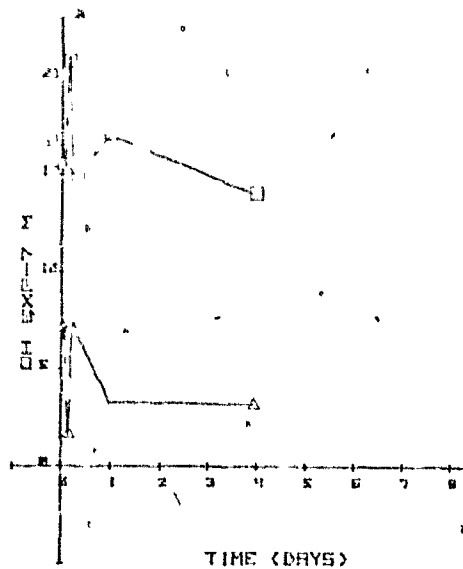
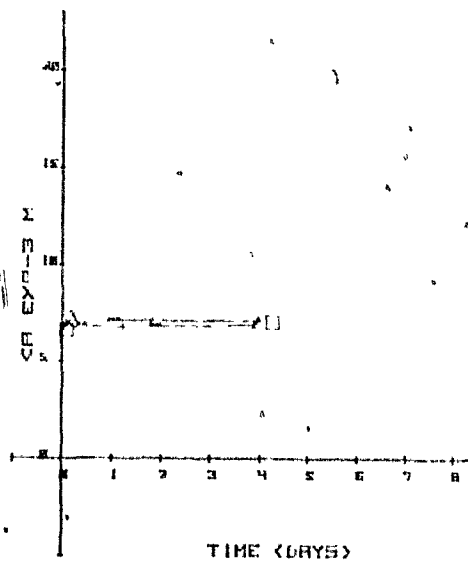
A study of the effect of higher temperatures on the kinetics of the Ontario apatite exposed to seawater spiked with 500 ppm NaF was made (Figure R59). The tests were car-

Effect of Higher Temperatures Combined with
the Effect of a 500 ppm NaF Spike on the
Dissolution of Ontario Apatite in Seawater (1atm.)

Figure R59

△ : 25°C

□ : 50°C



ried out at 25° and 50°C and 1 atmosphere. The increase in temperature significantly reduced the solubility of the apatite (in terms of total phosphate) compared to the results obtained for the spiked solution at 2°C and the unspiked solution at 25°C. However, the increase in temperature did not appear to cause a faster precipitation of CaF_2 , as the fluoride variation for the higher temperature experiments was essentially the same as for the 2°C experiment. Simpson (1969) has found that very high fluoride concentrations were necessary for the formation of fluoro-alkali apatites and that apatites formed above 30°C lacked good crystallinity.

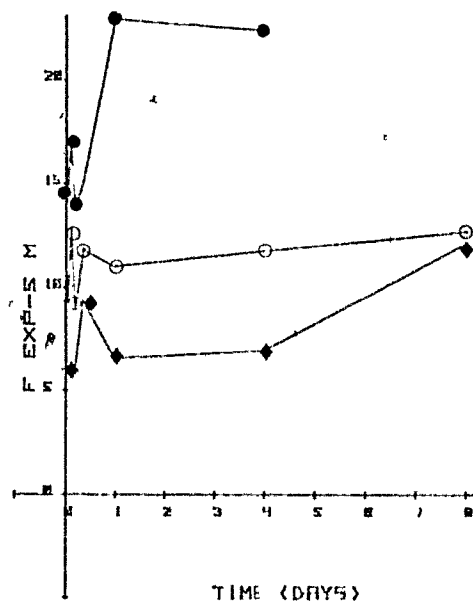
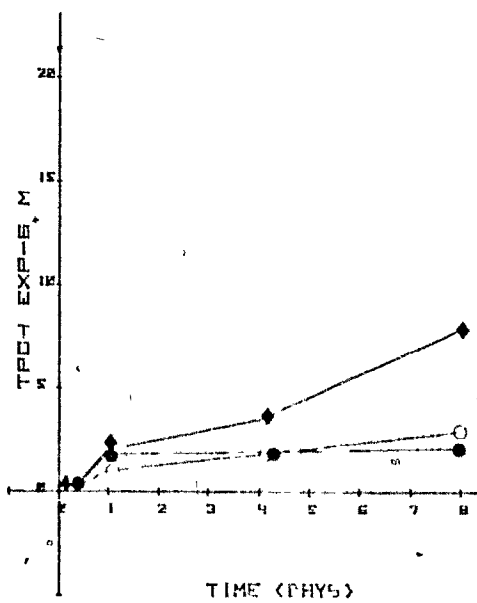
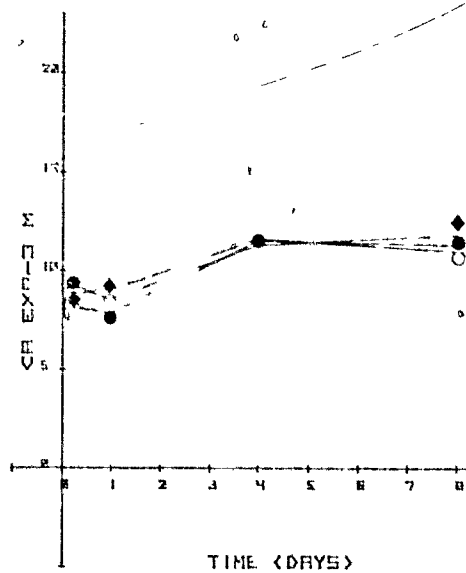
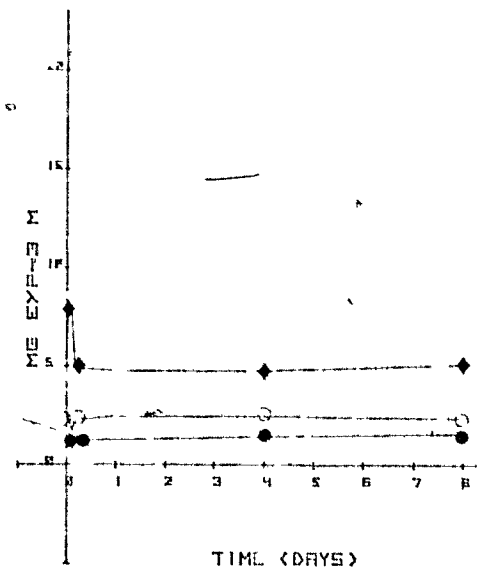
D.IV. Variation of Ca/Mg Ratios in Seawater

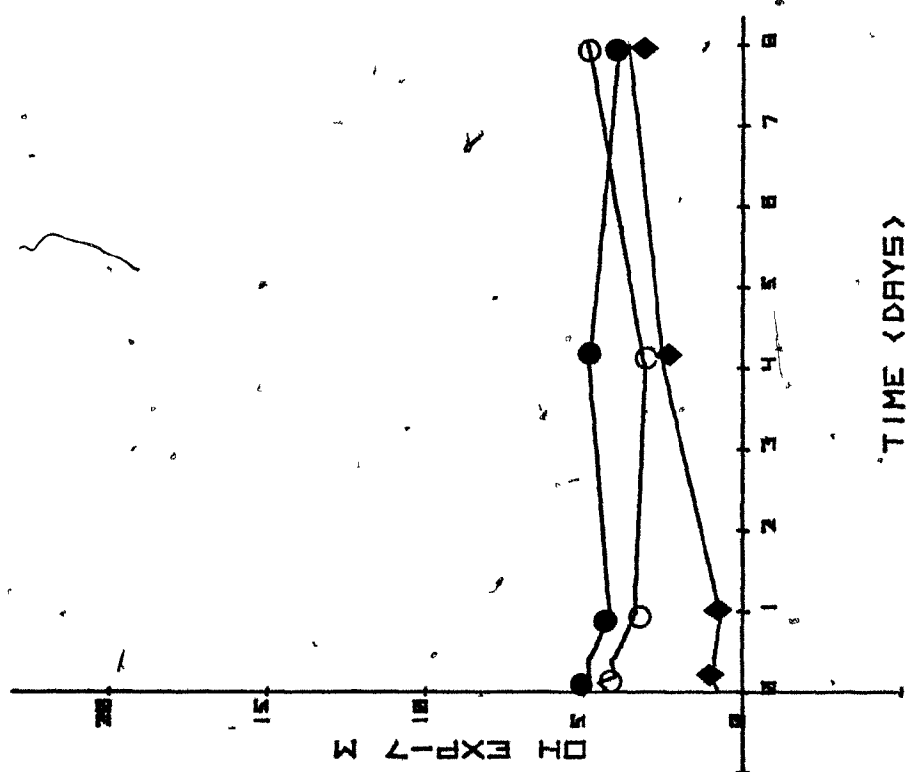
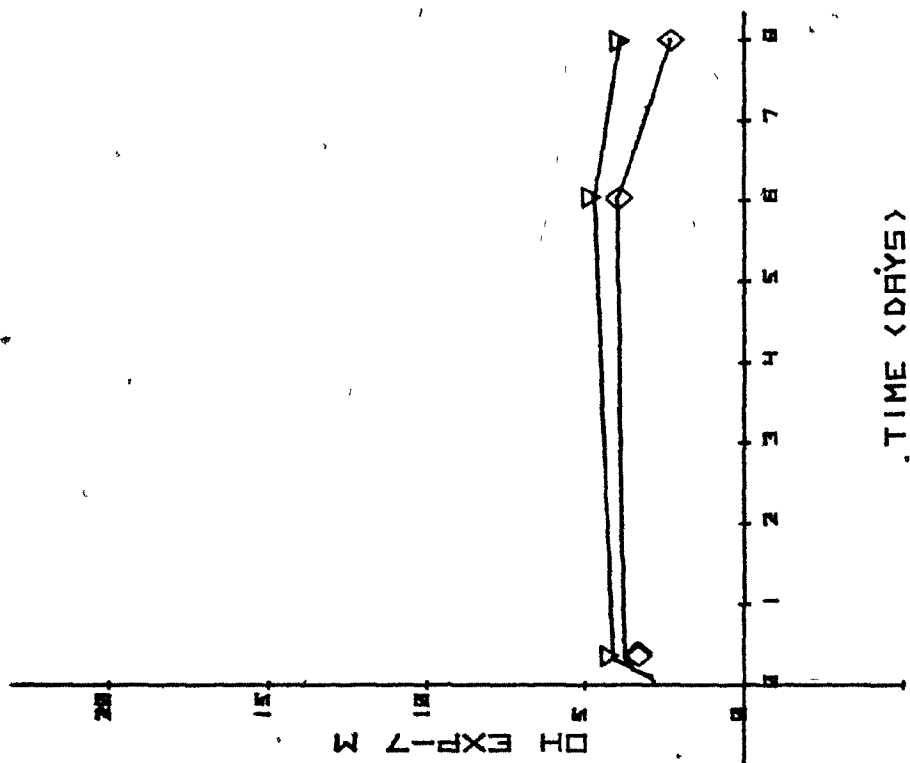
Martens and Harriss (1970) found that the magnesium content in seawater prevented the formation of crystalline apatite through the replacement of magnesium for calcium within the crystal structure. Simpson (1966), Bachra et al. (1964) and Tomazic et al. (1975) found that the presence of magnesium encouraged the formation of an amorphous calcium phosphate, possibly octa-calcium phosphate, rather than crystalline apatite. To test the effects on dissolution and to examine the type of surface phase, the solubilities of Ontario apatite in seawater/artificial seawater (Kester et al., 1967) mixtures giving Ca/Mg ratios of 0.03, 0.003, 2.5, 5, and 10 (1 atm., 2°C) (Figures R60-62 were determined).

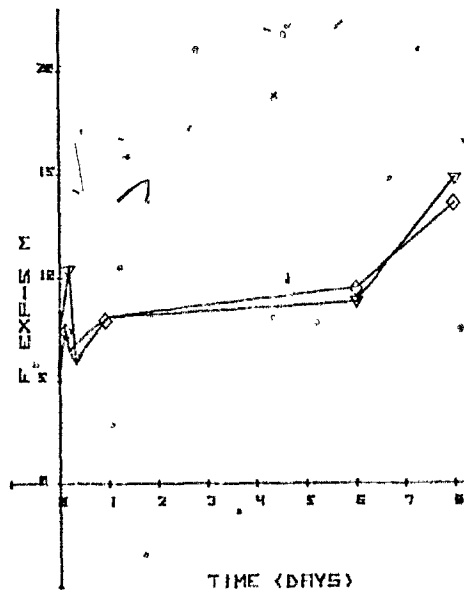
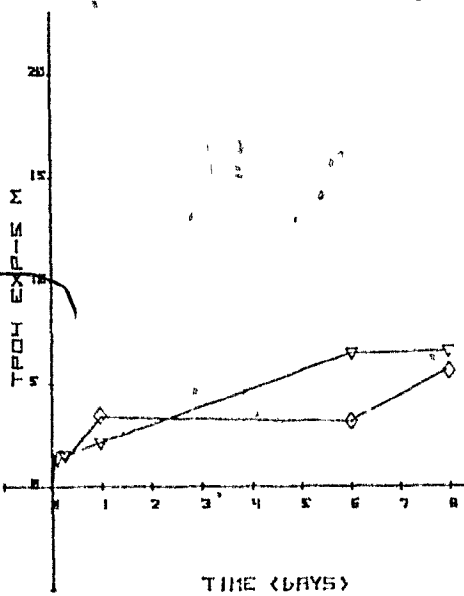
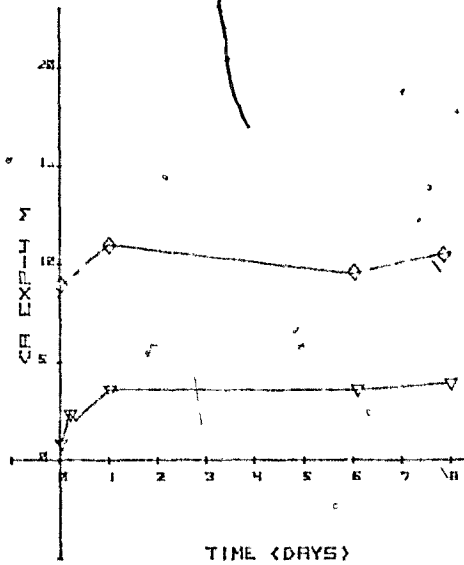
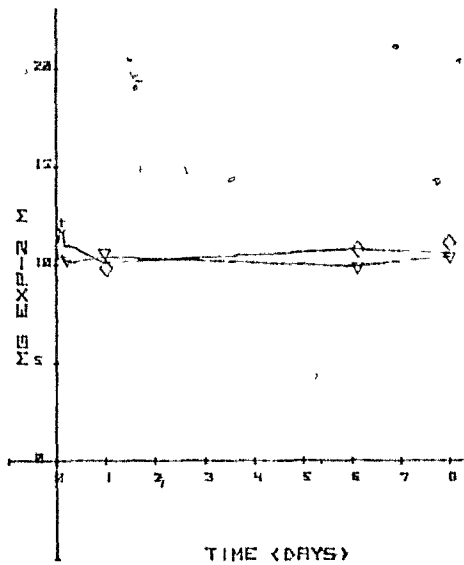
Effect of the Variation in Ca/Mg Ratios on the
Dissolution of Ontario Apatite in Seawater
(1 atm., 2°C)

Figures R60 - R62

- ◆ : Ca/Mg = 2.5
- : Ca/Mg = 5
- : Ca/Mg = 10
- ◇ : Ca/Mg = 0.03
- ▽ : Ca/Mg = 0.003







In the cases of low calcium levels (Figures R60/61) there was a decrease in the rate of dissolution compared to the rate in regular seawater, but after 8 days the phosphate and fluoride levels were about the same as in the regular seawater experiments. No change could be seen in the magnesium levels.

In the low magnesium experiments (Figures R61/62), total phosphate was significantly reduced compared to regular seawater experiments. This indicates that the presence of magnesium tends to promote dissolution of apatite, possibly through the formation of strong ion-pairs with the phosphate species and fluoride. The initial solid reaction may be the exchange of magnesium for calcium or the introduction of magnesium into the crystal structure in "calcium" vacancies on the surface. This new magnesium phase may be fairly soluble compared to apatite. Simpson (1966) has reported on the formation of a magnesium-containing amorphous phase.

D.V. Variations in Total CO_2

Since some apatites are known to contain carbonate within the apatite structure (McConnell, 1973); variations in the carbonate content of the seawater may effect the solubility. There was a change in experimental procedures here, with the use of 50 g samples in 1000 cc solutions.

11 atm., 2°C). Ontario (1.70 wt. % CO₂) (Figure R63/64) and Mexican (1.16 wt. % CO₂) (Figure R64/65) were used.

Variations in TCO₂ for both the Mexican and Ontario apatites showed essentially no change over the length of time of the experiment. However, the strong changes in the OH₂ content indicated a change in the speciation of the carbonate species in solution during the experiment. If a carbonate-apatite phase did form during the early stages of reaction, it was likely to re-dissolve rapidly, because of the weak carbonate linkages within the apatite structure (LeGeros et al., 1967, a,b). Simpson (1966 b) found that in the presence of small amounts of chloride or fluoride, even large quantities of CO₂ in solution are likely to yield apatite rather than other calcium phosphates.

E. Pretreated Apatite Reactions with Unspiked Seawater

E.I. Pretreatment in Regular Seawater

If a new surface phase is formed when an apatite is exposed to seawater, then subsequent exposures to seawater should show a difference in the concentration changes in solution relative to the original seawater.

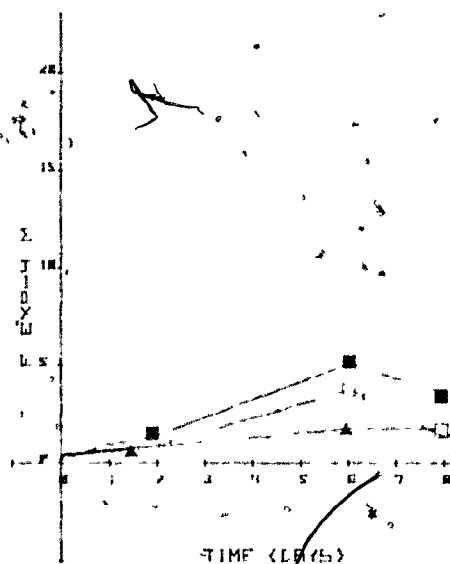
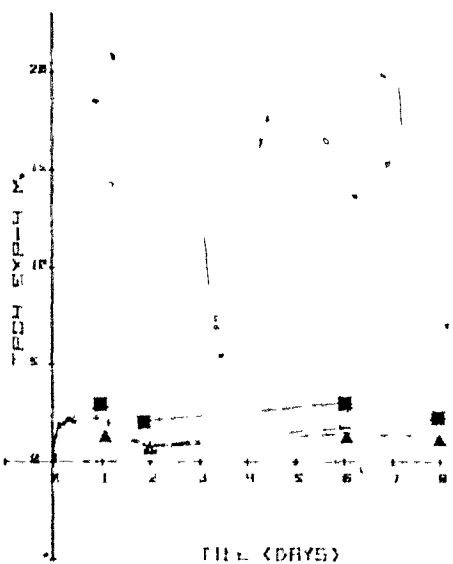
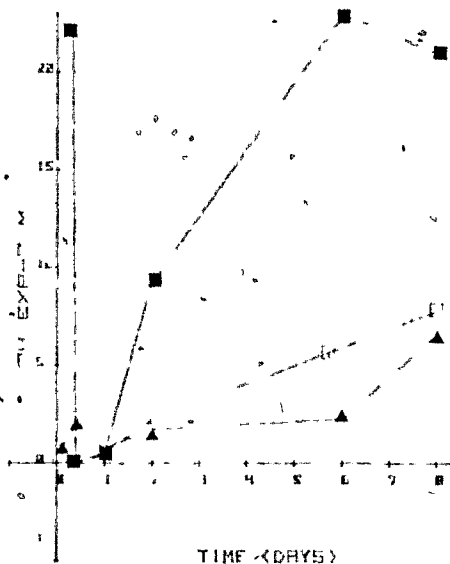
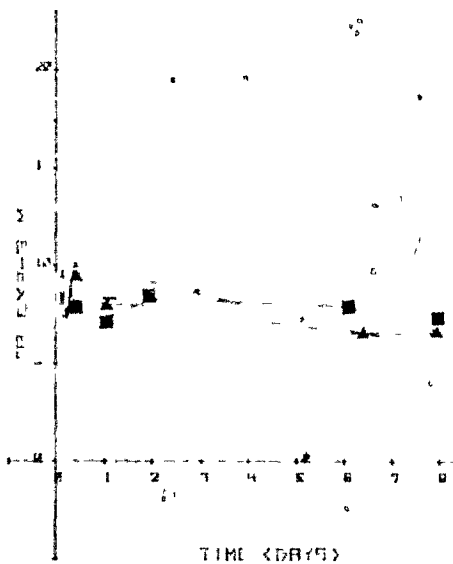
Figures R66-68 illustrate changes in solution when an apatite is repeatedly re-equilibrated with fresh seawater. Mexican, Florida and Marine apatites were used and each experimental period lasted eight days (1 atm., 2°C).

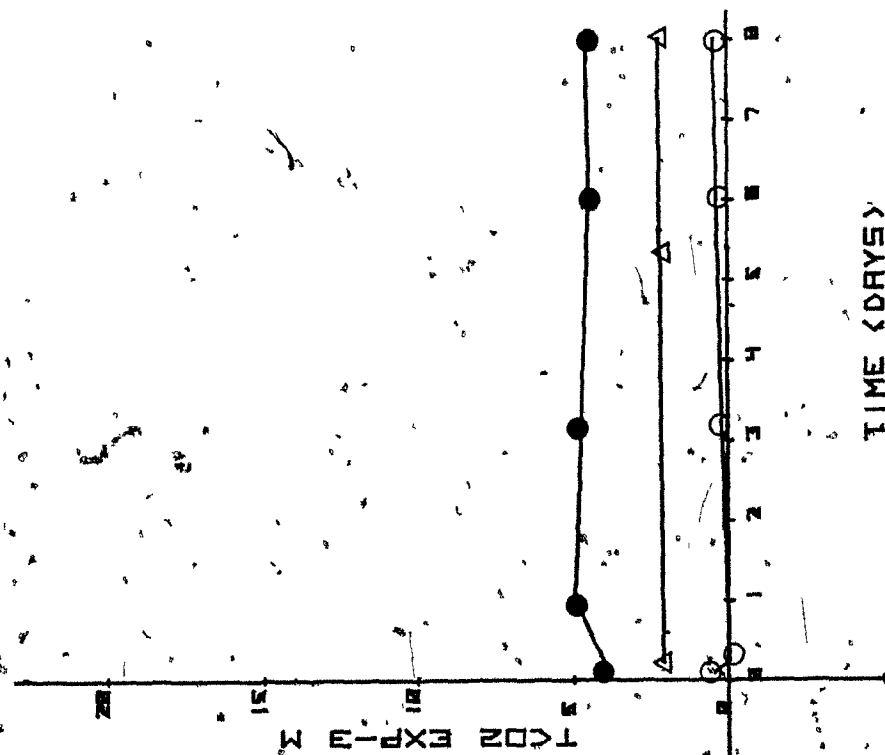
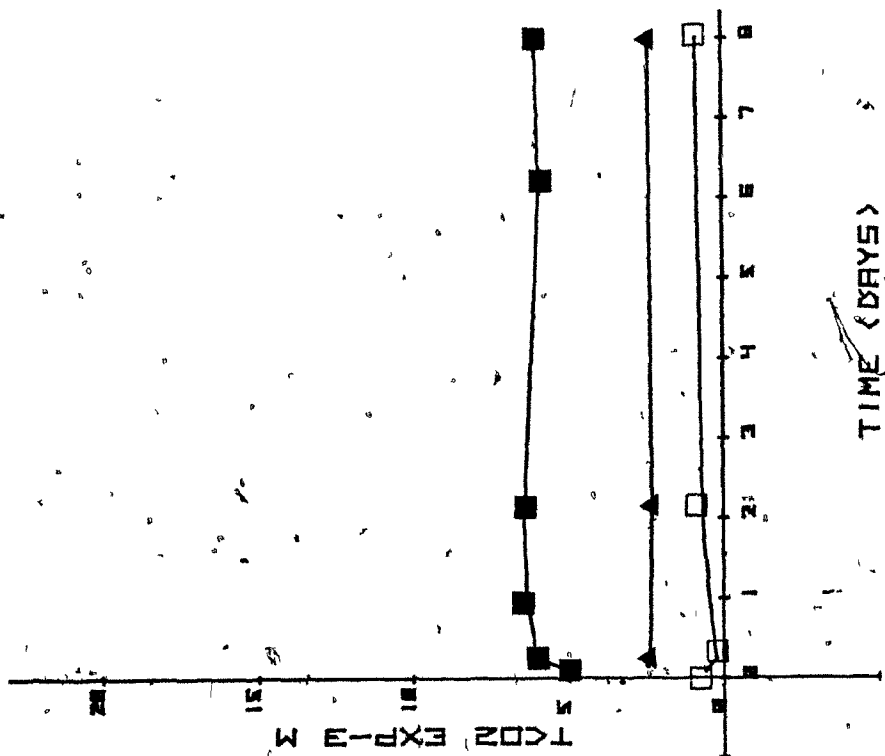
Effect of Variation of Total CO_2 in Solution
on the Dissolution of Apatite in Seawater

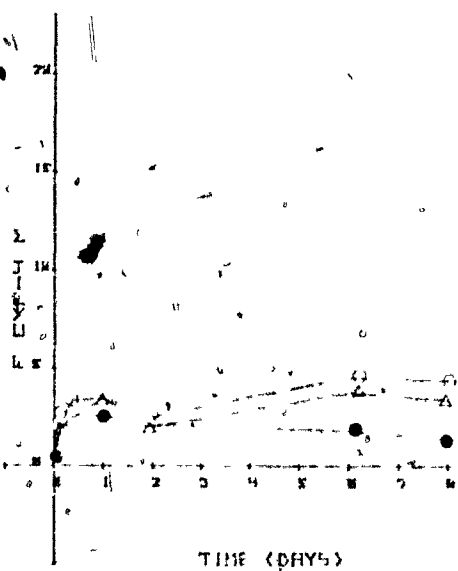
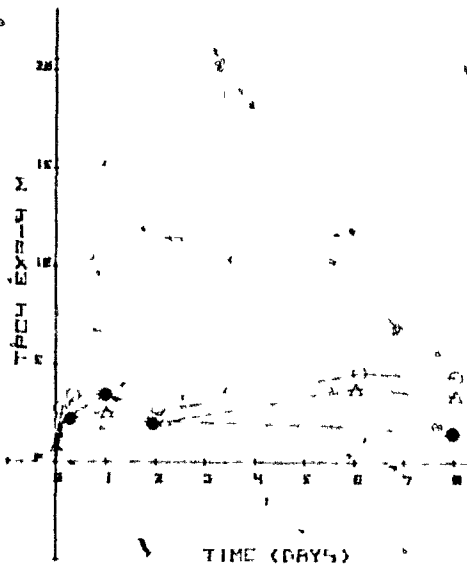
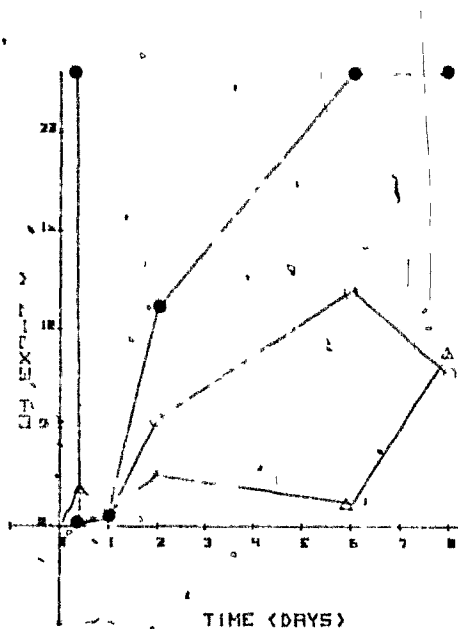
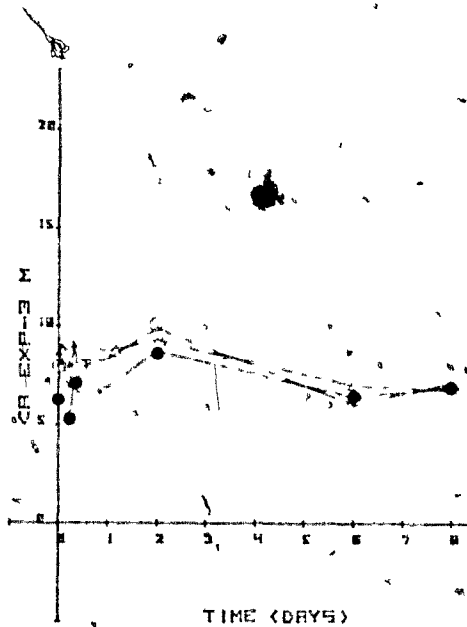
Figure P63/64: Ontario

R64/65: Mexican

- : High Concentration TCO_2
- △ : Unspiked Seawater Ontario
- : Low Concentration TCO_2
- : High Concentration TCO_2
- ▲ : Unspiked Seawater Mexican
- : Low Concentration TCO_2







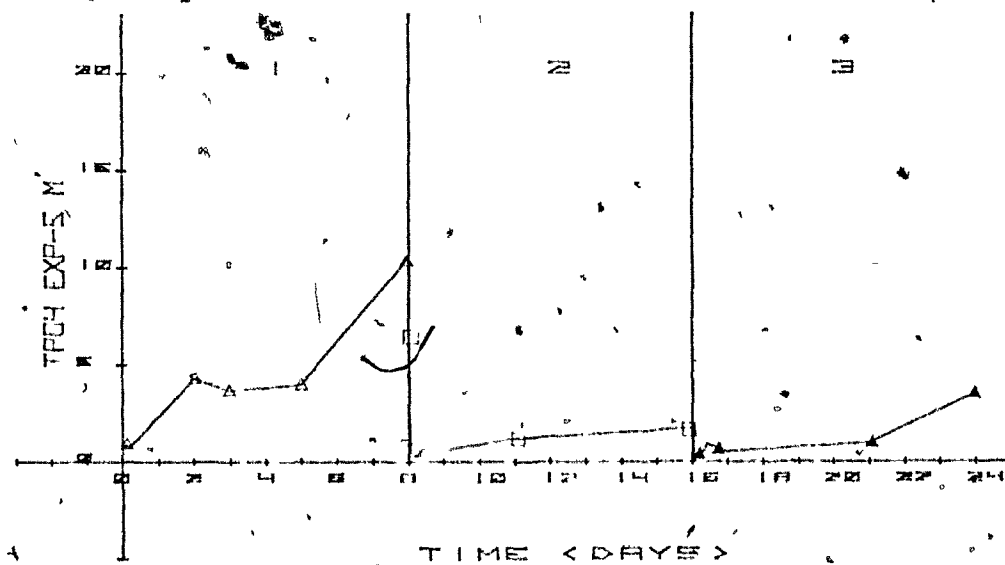
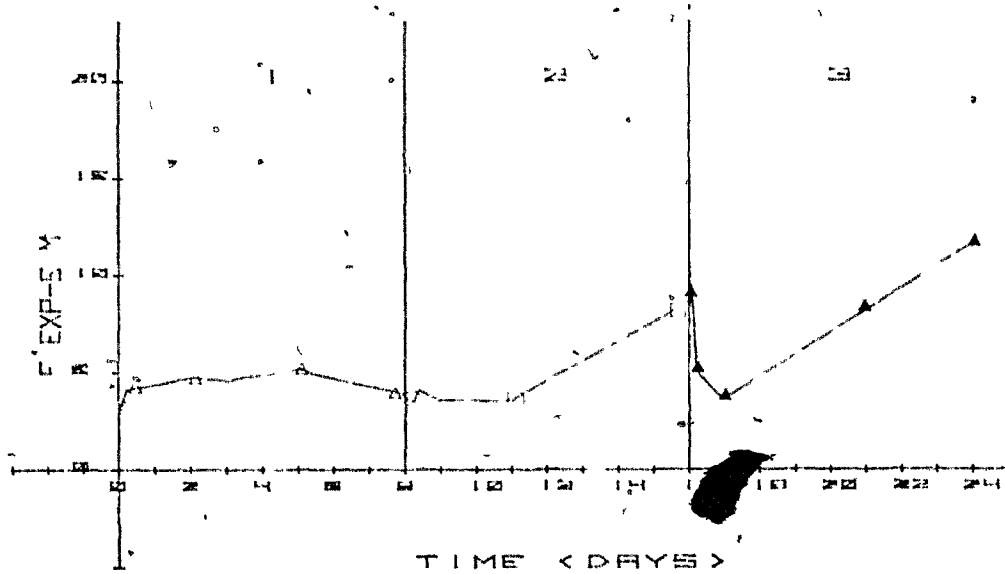
Effect of Pre-Exposure in Seawater on the
Dissolution of Apatite in Seawater (1 atm., 2°C)

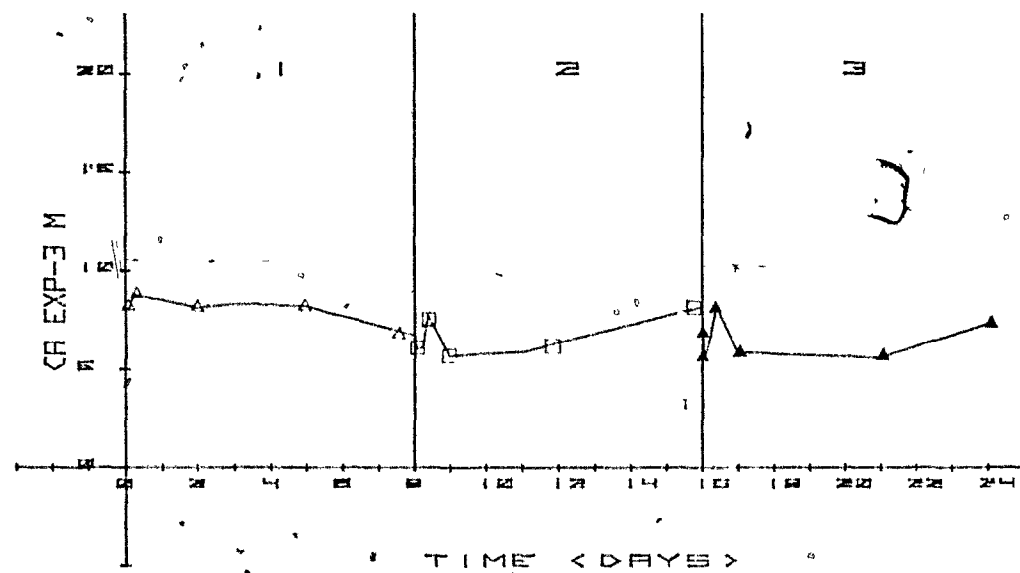
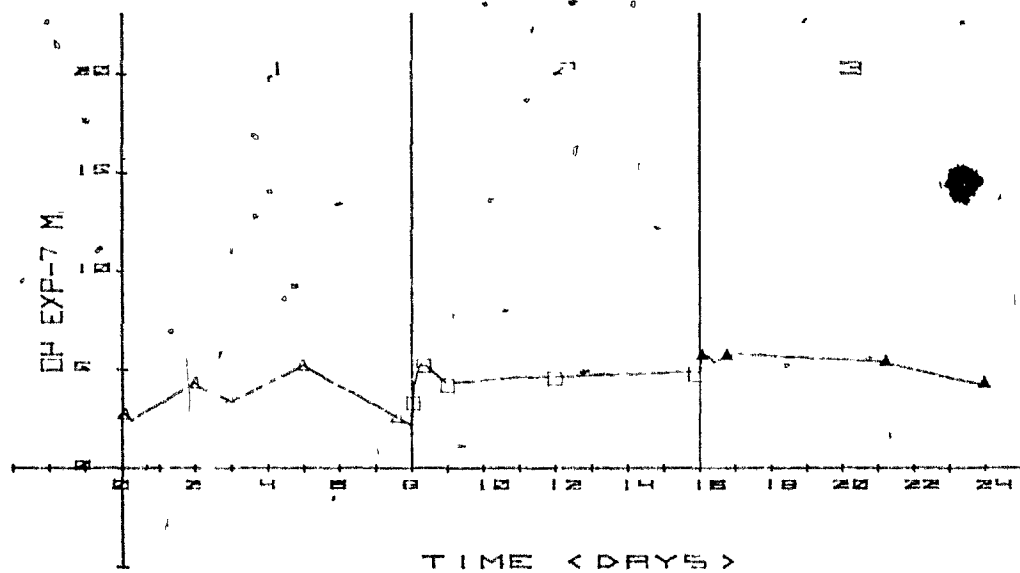
Figure R66: Mexican

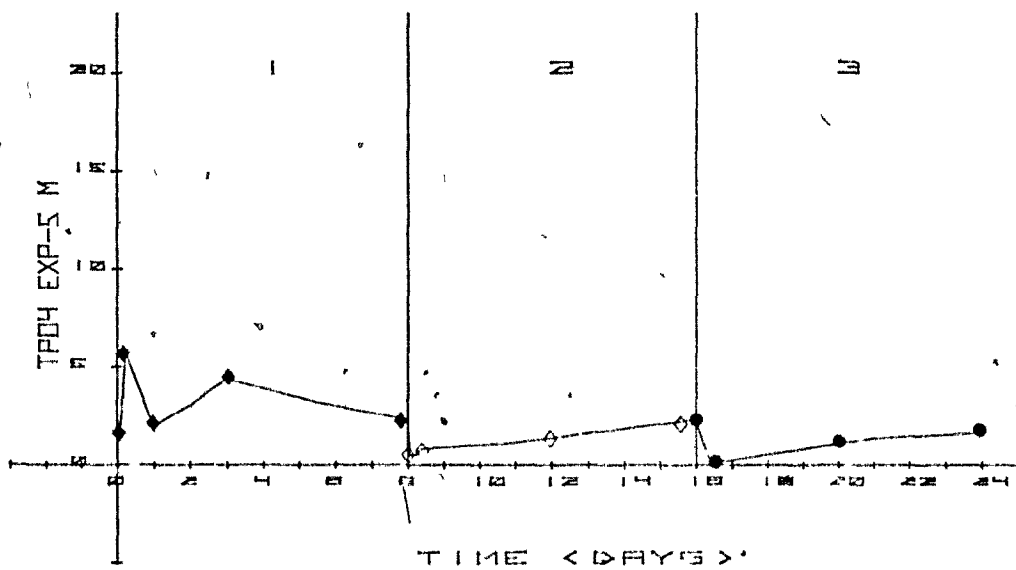
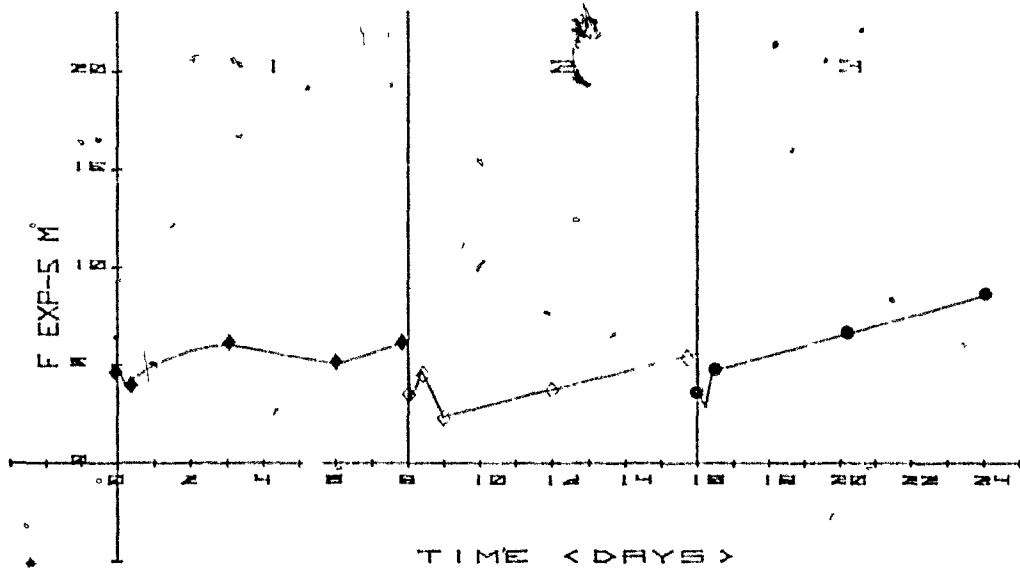
R67: Florida

R68: Marine

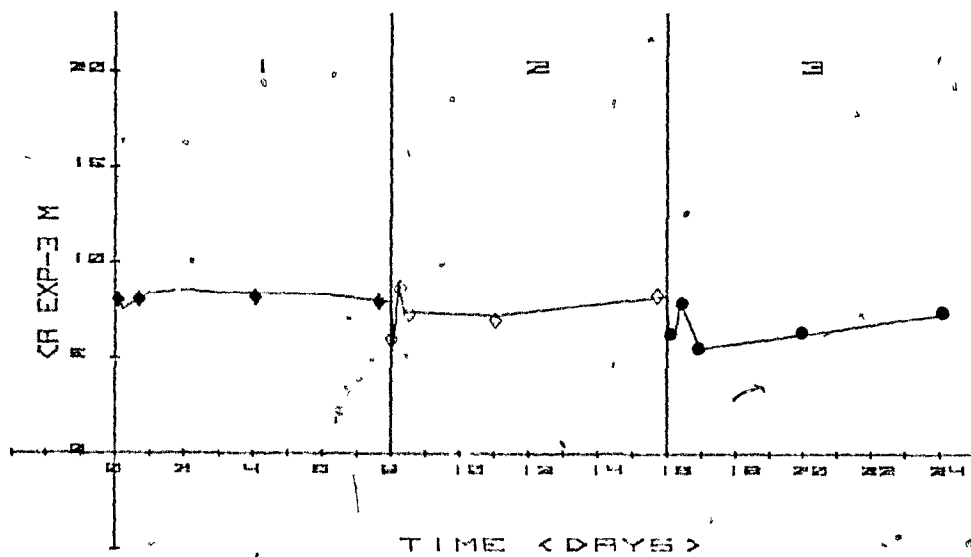
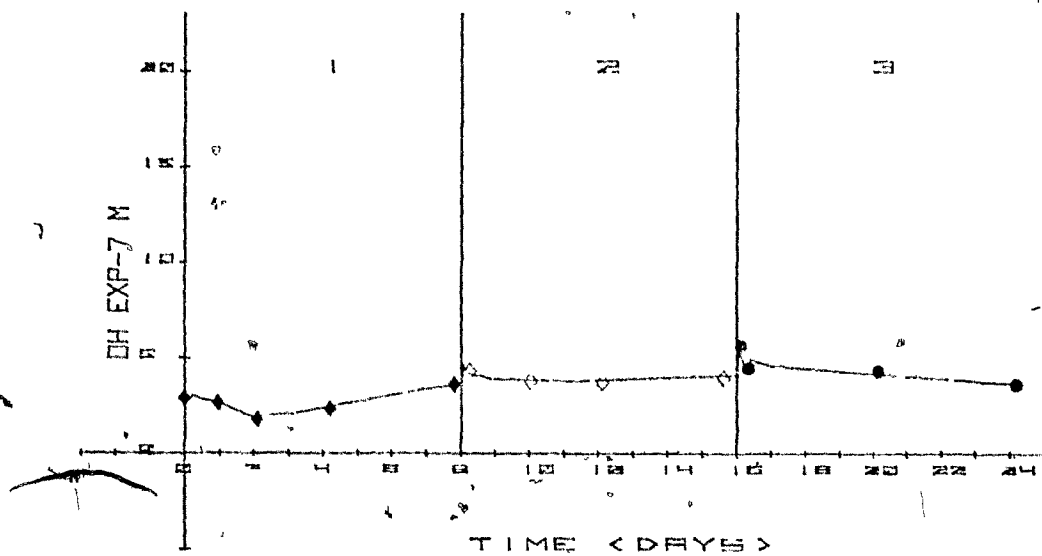
	Mexican	Florida	Marine
First Period	△	◆	▽
Second Period	□	◇	▼
Third Period	▲	●	○

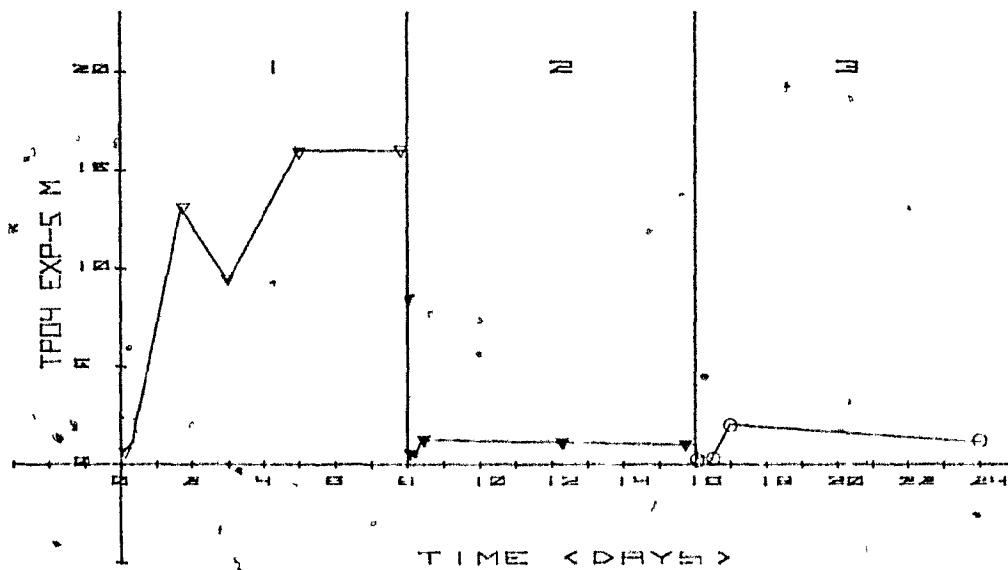
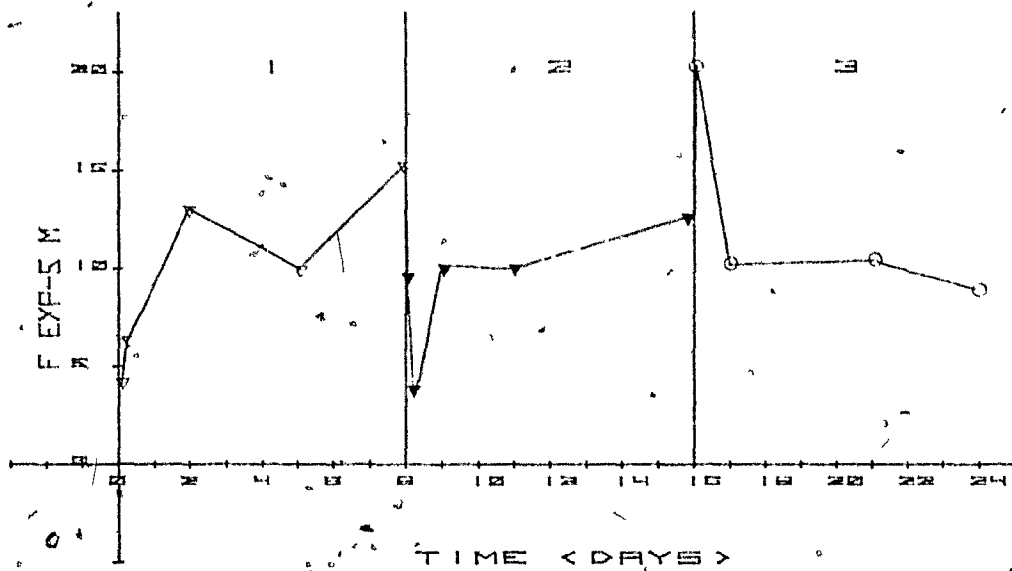


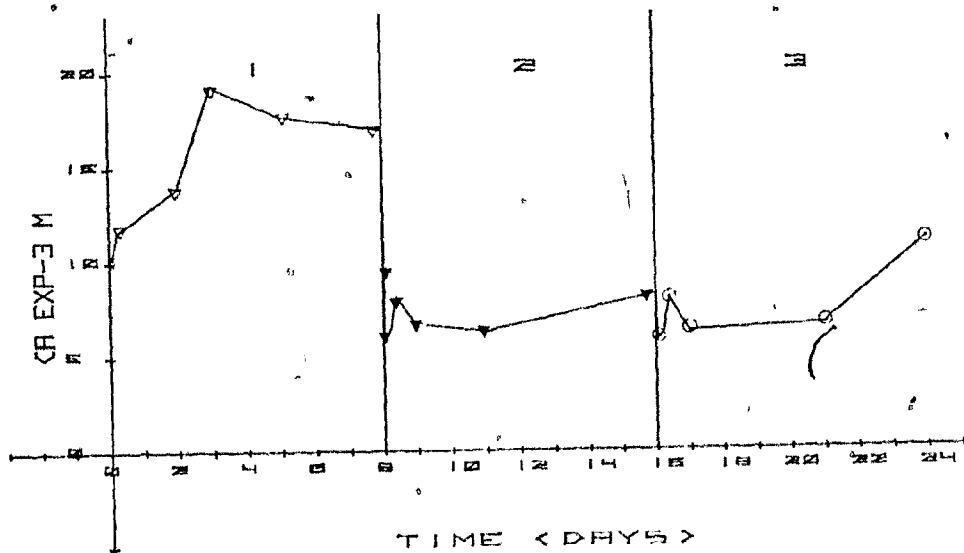
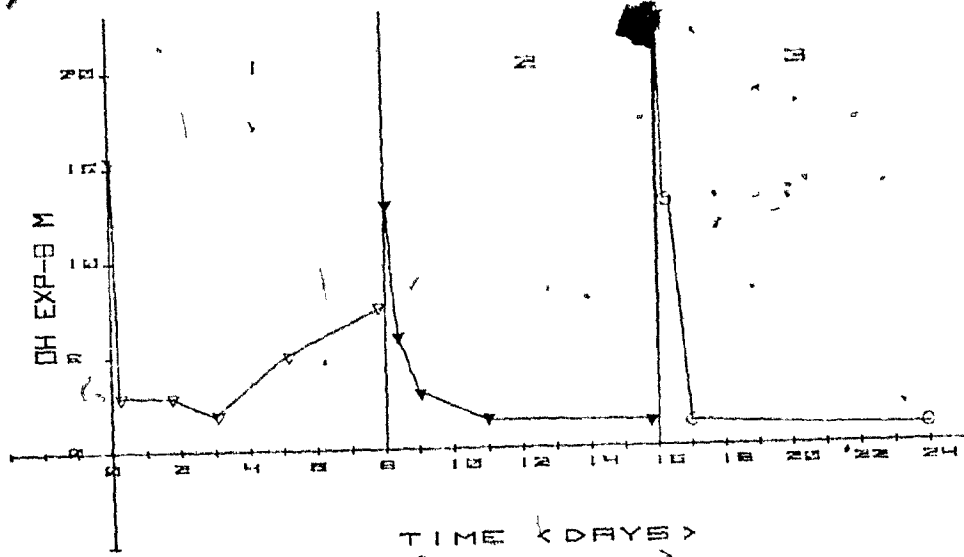




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In the Mexican apatite case (Figure R66), the phosphate concentration definitely decreased comparing the second to the first period. There was a slight further drop at the beginning of the third period, but a steady concentration, approximately equivalent to that obtained in the second period, was soon achieved. The fluoride level did not begin to change significantly until late in the second period and steady dissolution proceeded throughout the third period. The calcium concentration showed essentially no change over the three periods. The differences in behavior of three main species indicates incongruent dissolution. During the first period a loosely-bound high phosphate surface layer is dissolved. A more strongly held secondary layer, probably a more pure fluoroapatite with a lower solubility, takes longer to dissolve and the effects of this dissolution are not seen until late in the second period.

The behavior of the Florida apatite (Figure R67) is much the same as the behavior of the Mexican apatite. The slight differences can be seen in the phosphate levels in the first period, indicating a less-soluble surface phase on the Florida apatite. This may be due to the higher bulk fluoride content of the Florida apatite.

The Marine apatite (Figure R68) shows a significant loss of phosphate during the first period. Subsequent periods indicated the formation of a fairly stable surface layer as

phosphate levels remained low and steady. There was also a slight drop in calcium, indicating that the surface was a loosely held calcium phosphate, possibly a carbonate form.

E.II. Pretreatment in Phosphate-Spiked Seawater

The solubilities of Mexican and Florida (Figures R69/70) apatites which had been first exposed to seawater spiked with 25 and 50 micromolar phosphate (1 atm., 2°C, 8 days) were determined in regular seawater (1 atm., 2°C). There is a noticeable difference in the behavior of the two apatites. In the Mexican case the phosphate-pretreated samples showed essentially no dissolution, while the sample pretreated in regular seawater showed dissolution. In the Florida case, all three samples showed dissolution. In terms of phosphate, the dissolution increased in the order 50 > 25 > regular. Obviously a phosphate complex formed on the Mexican apatite was fairly insoluble. The phosphate was probably only adsorbed onto the surface of the Florida apatite and this was rapidly released back into the solution when fresh seawater was exposed to the pretreated apatite.

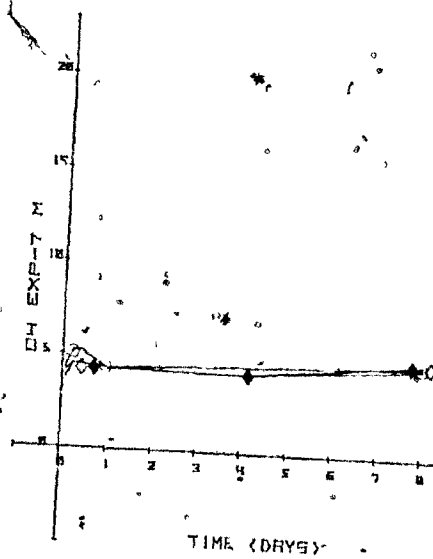
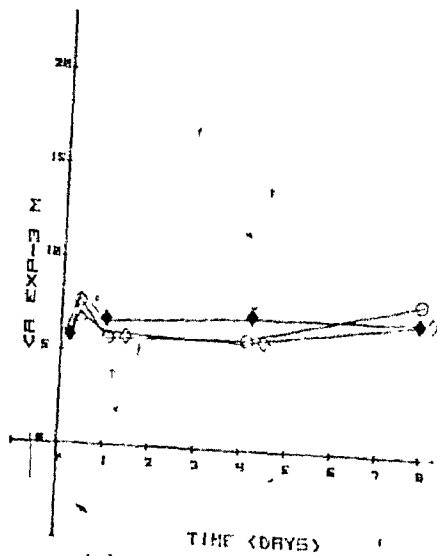
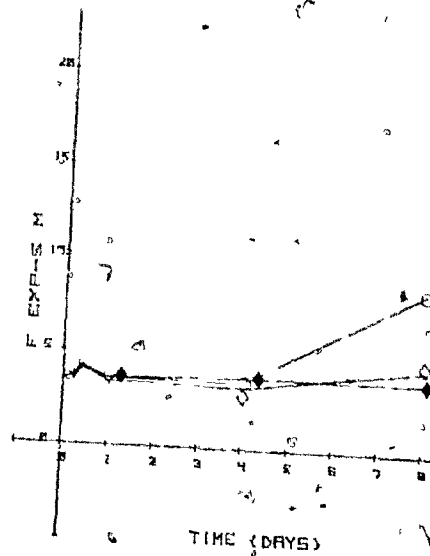
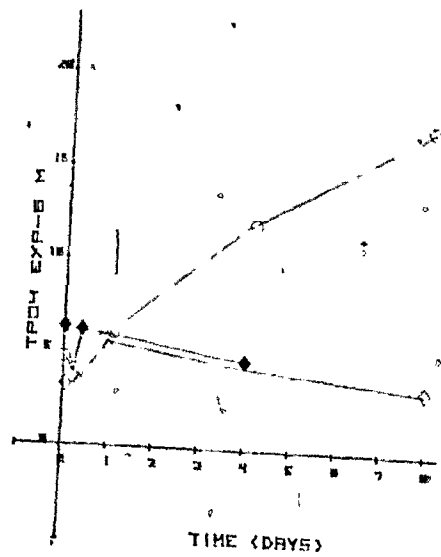
E.III. Pretreatment in 500 ppm Fluoride-Spiked Seawater

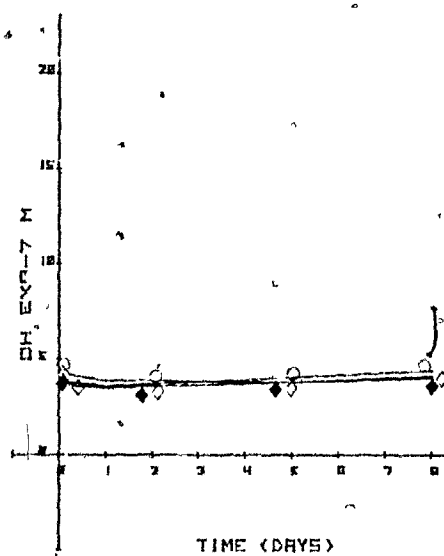
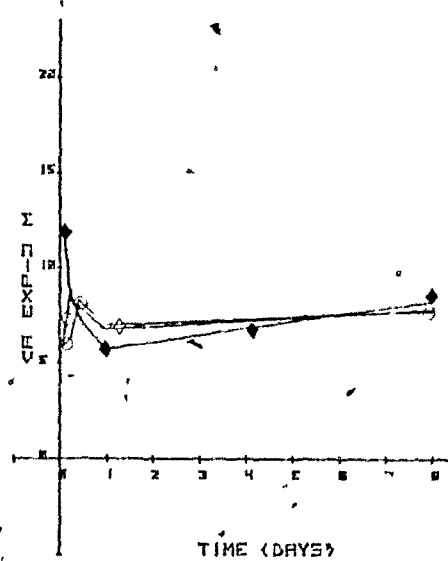
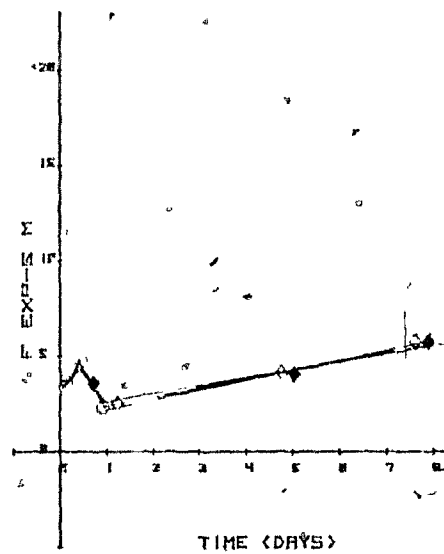
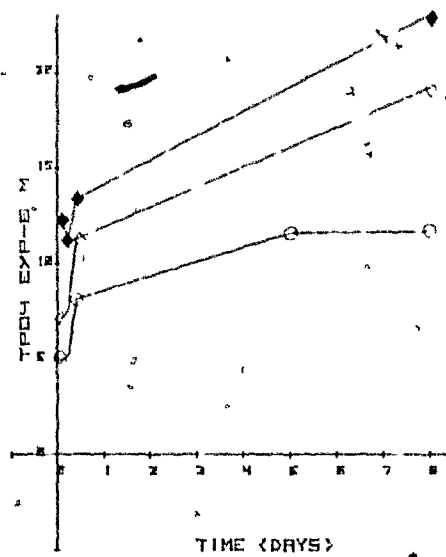
The solubilities of Mexican (Figure R71) and Ontario (Figure R72) apatites that were first exposed to seawater spiked with 500 ppm NaF (1 atm., 2°C, 8 days) were measured

Effect of Pre-exposure in Phosphate-Spiked
Seawater on the Dissolution of Apatite in
Seawater (2°C, 1 atm.)

Figure R69: Mexican
R70: Florida

- ◇ : Pre-exposed to 2.5×10^{-5} M phosphate-Spiked Seawater
- ◆ : Pre-exposed to 5×10^{-5} M phosphate-Spiked Seawater
- : Pre-exposed to Unspiked Seawater



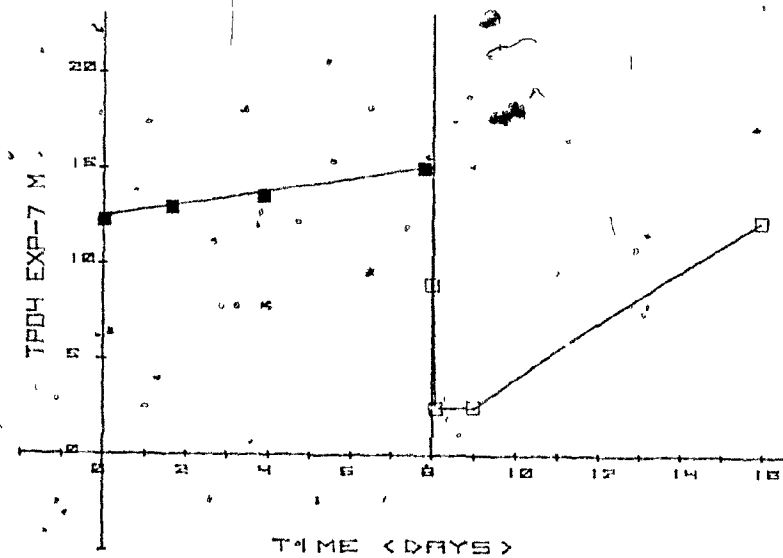
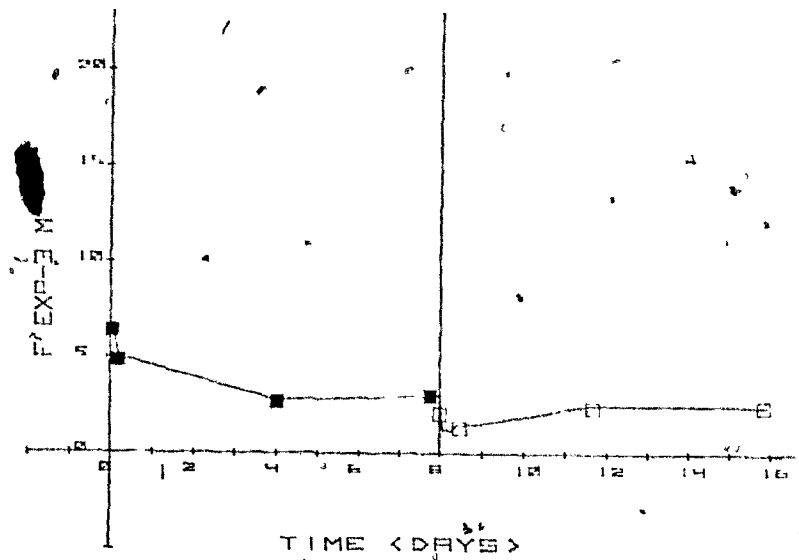


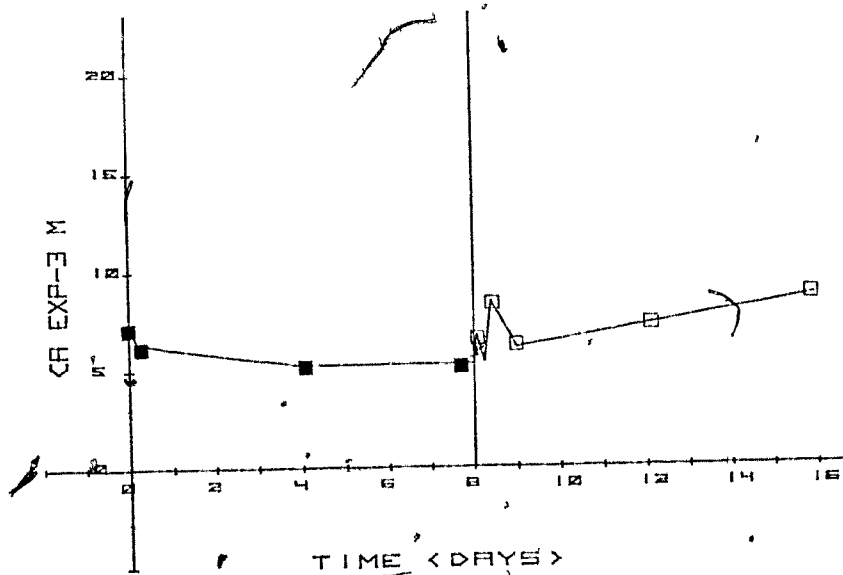
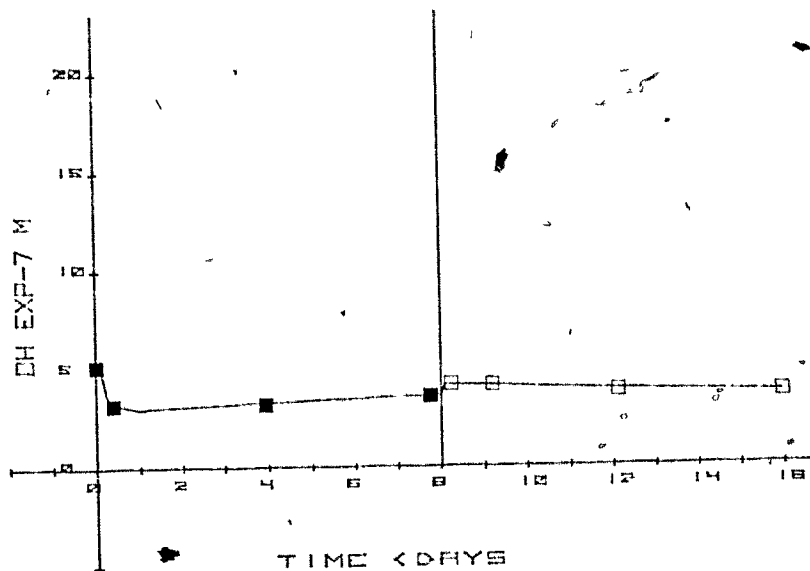
Effect of Pre-exposure in 500 ppm NaF Spiked
Seawater on the Dissolution of Apatite in
Seawater (1 atm., 2°C)

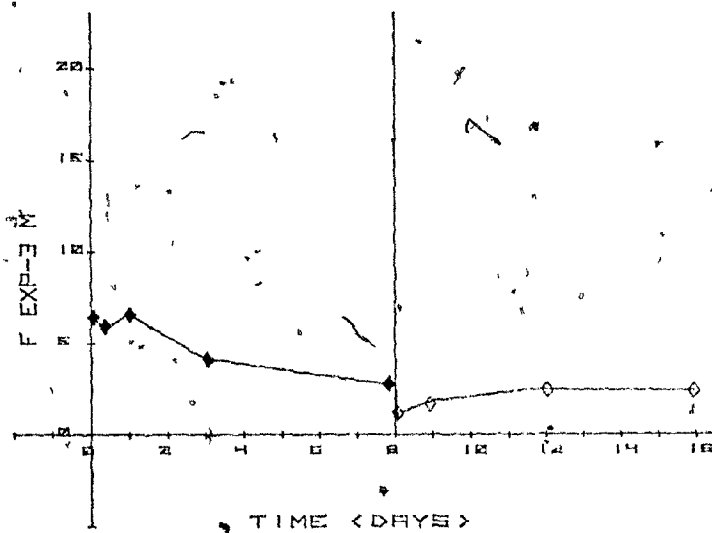
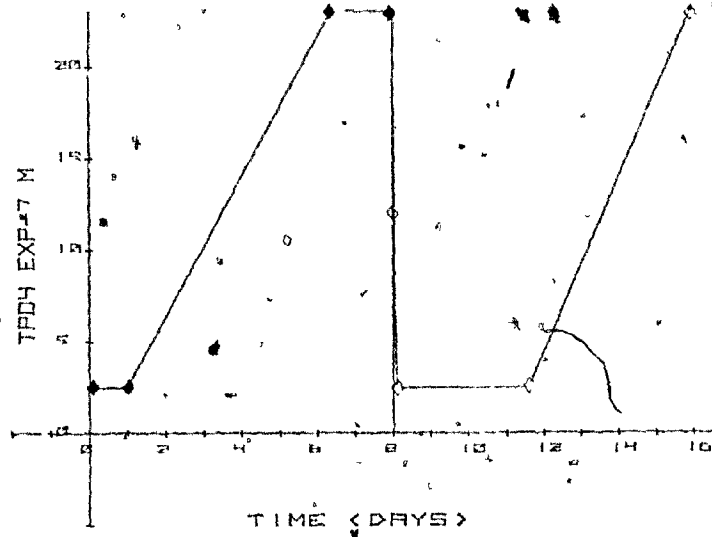
Figure R71: Mexican

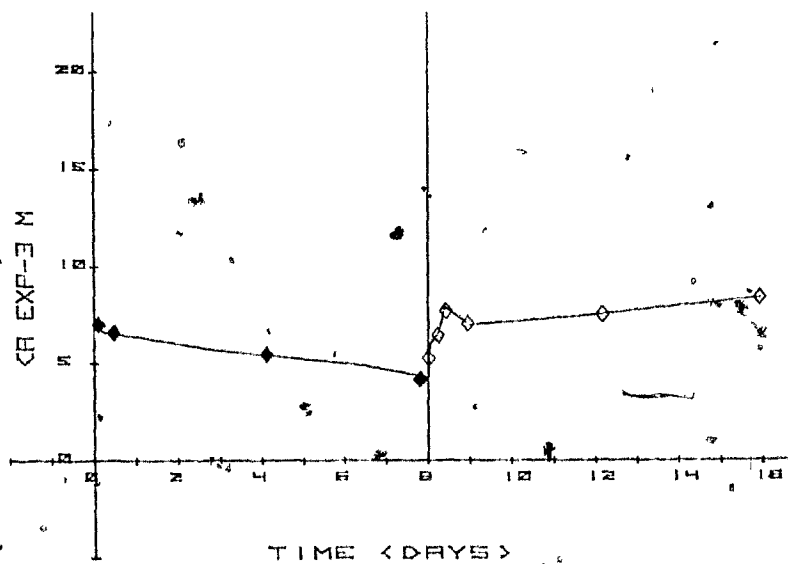
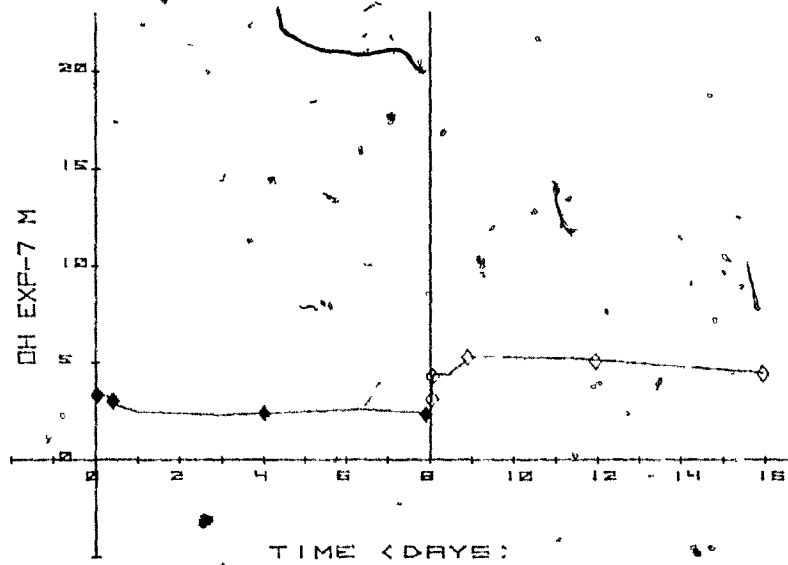
R72: Ontario

	Mexican	Ontario
Unspiked Seawater	□	◆
Spiked Seawater	■	◇









in regular seawater (1 atm., 2°C). The first period on the graphs illustrates the behavior of the apatites during the pretreatment period. For both apatites, there is an uptake of fluoride and to a lesser extent calcium, while the phosphate level is significantly less than when the initial solution was regular seawater. Exposure to fresh seawater during the second period shows a slow increase in fluoride in solution, back to about the concentration level at the end of the first period. Phosphate levels remain low and not until late in the second period is there significant increase in phosphate in solution. This would probably indicate the formation of both CaF_2 and a fluoro-apatite on the surface of the apatite. This new layer re-dissolves during the second period and this produces the increase in dissolved phosphate during this period. However, the levels of fluoride and calcium still remain fairly high, indicating that CaF_2 and fluorapatite could be re-forming during the second period. The increasing amounts of dissolved phosphate during the late second period might tend to inhibit CaF_2 formation. Electron micrographs (Figure R13) of the solid after the second period, however, still indicate the presence of CaF_2 crystals of the surface.

F. Variations of Surface Area of Apatites

F.I. Variation of Particle Size

Solubilities of unground and two sizes of ground (8-28

and 48-60 mesh) Marine apatite were measured in regular seawater (1 atm., 2°C) (Figure R73). The unground material was tested as 100g/1000 cc, while the ground samples were tested as 10g/100 cc. For both of the ground samples there was slightly higher levels of phosphate and calcium in solution compared to the unground sample. The increased calcium could be due to dissolution of calcium carbonate shells within the Marine apatite sample that were exposed to solution when the sample was ground. Fluoride levels in solution were essentially the same for the three samples, but there was some uptake from solution by the ground samples in the early part of the exposure period.

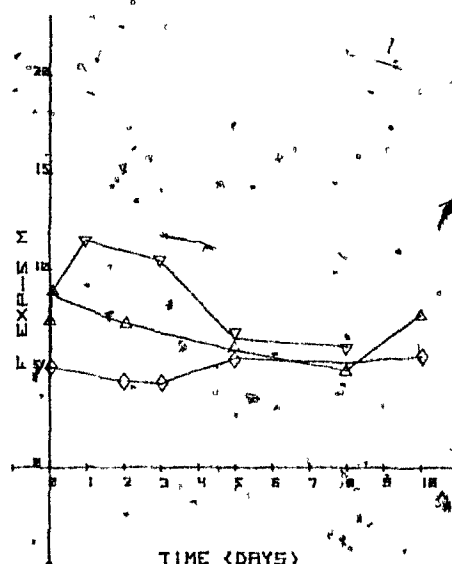
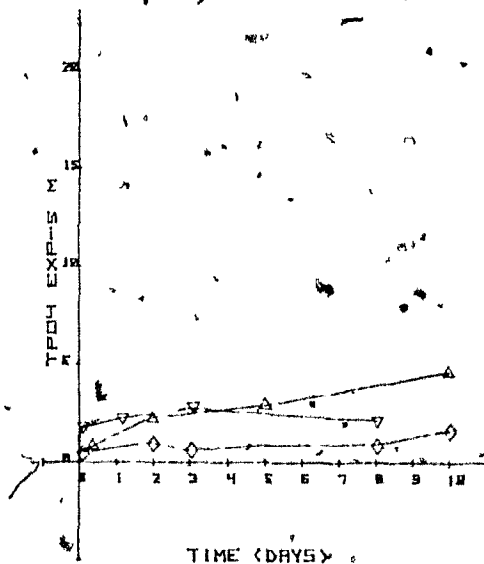
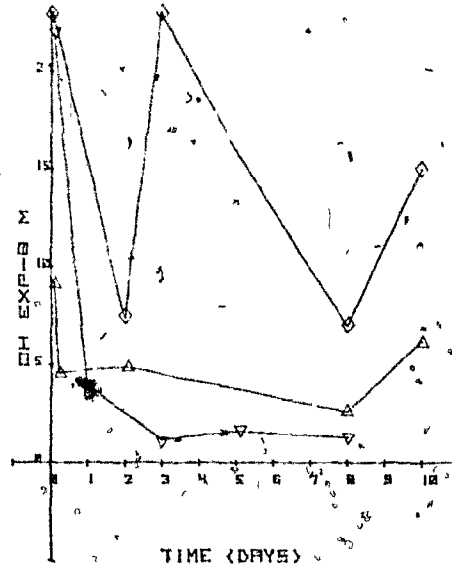
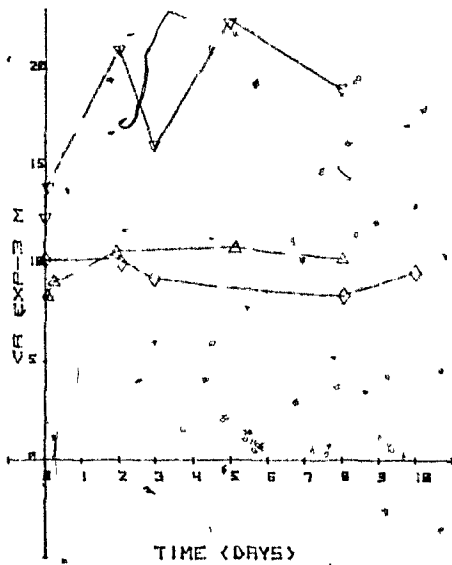
F.II. Variation of Solid/Solution Ratio

The solubilities of various weights (0.1, 0.5, 1, 5, 10g) of 8-28 mesh Mexican apatite were determined in 100 cc of seawater (1 atm., 2°C) (Figure R74). In terms of fluoride and calcium, there appeared to be no difference in the behavior of the five quantities. The only noticeable difference was in the total dissolved phosphate, where the behavior of the 0.1, 0.5, and 1 g quantities was essentially the same. The 5 g sample released about twice as much phosphate as the smaller quantities and the 10 g about twice as much as the 5 g quantity.

Effect of Grinding During Sample Preparation
on the Dissolution of Marine Apatite in
Seawater (1 atm., 2°C)

Figure R73

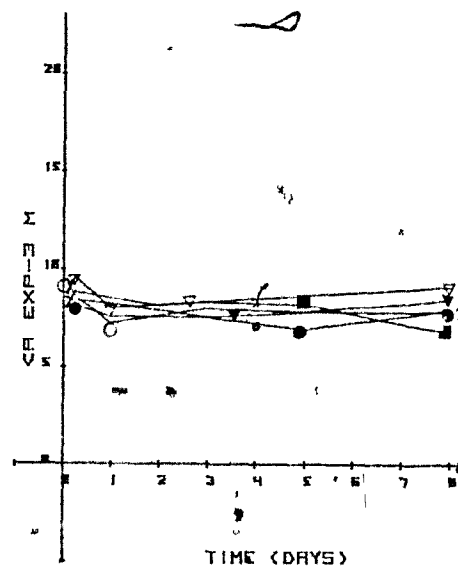
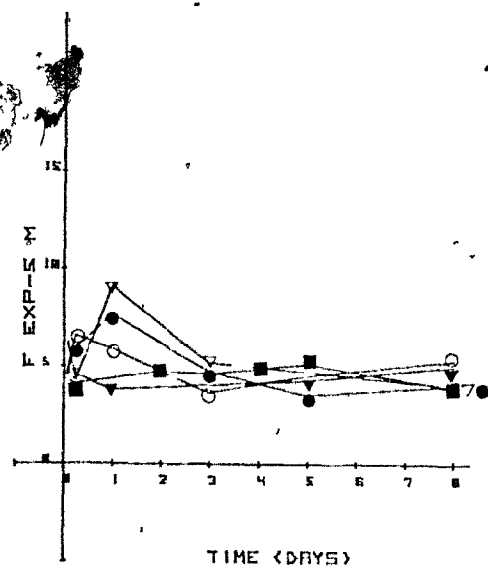
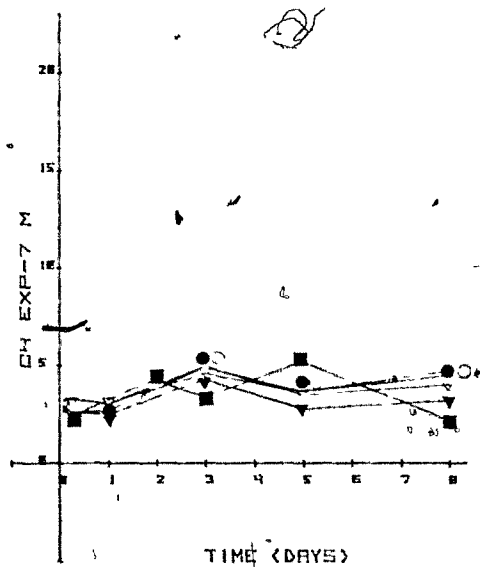
- ◇: Unground
△: Ground to 8-28 mesh
▽: Ground to 48-60 mesh

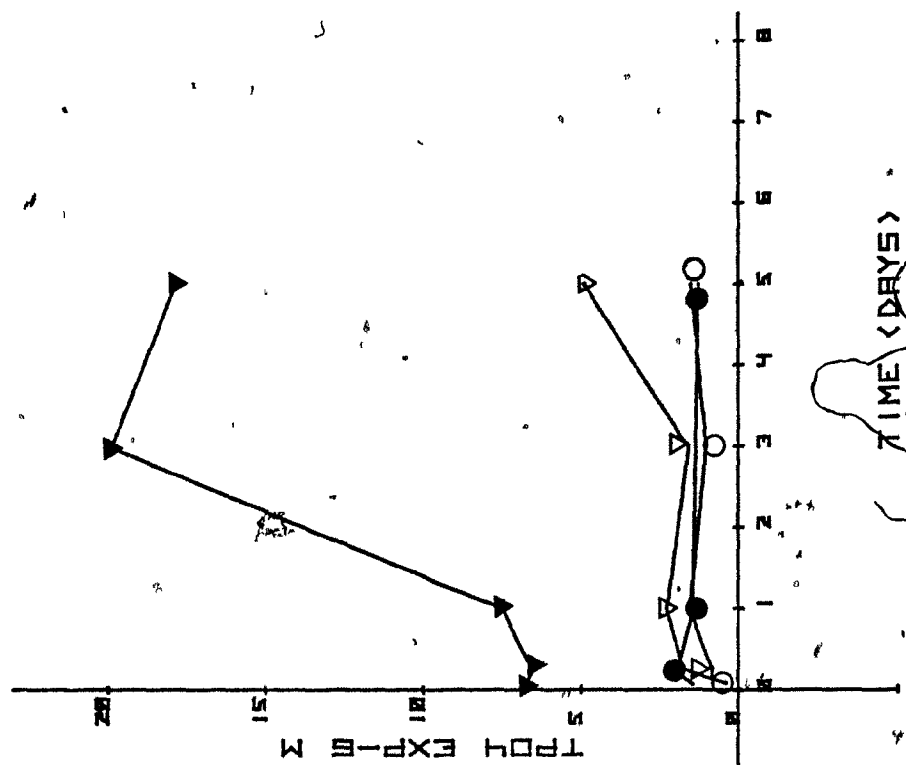
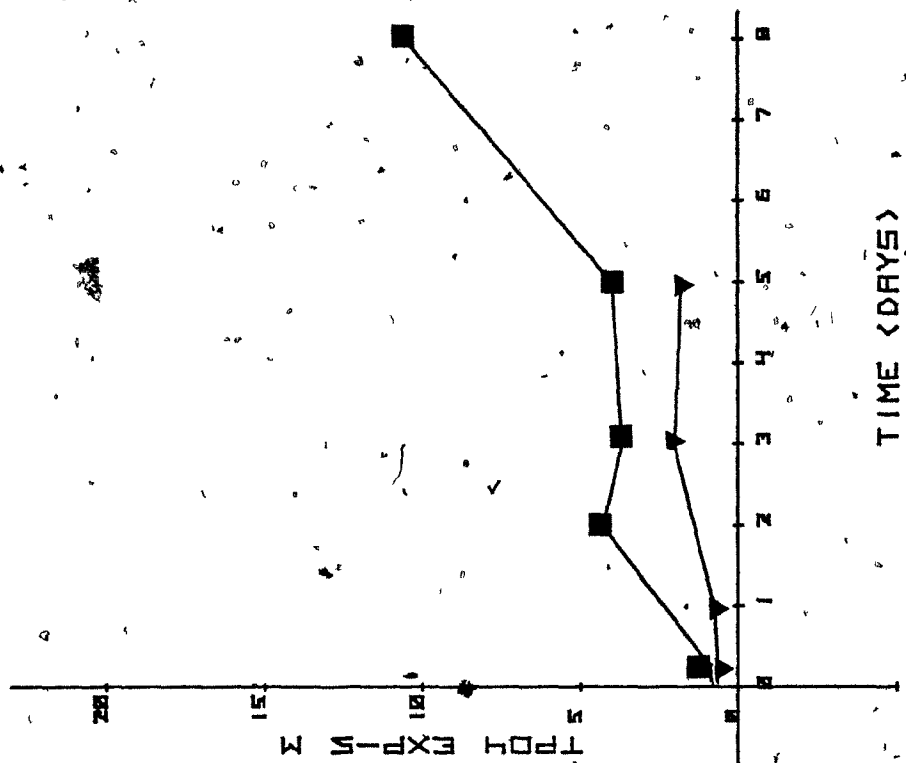


Comparison of the Effect of Variation of
Solid/Solution Ratio on the Dissolution of
Mexican Apatite in Seawater (1 atm., 2°C)

Figure R74/

- : 0.1 g/100cc
- : 0.5 g/100cc
- ▽ : 1 g/100cc
- ▼ : 5 g/100cc
- : 10 g/100cc





DISCUSSION

I. Dissolution Processes at 1 Atmosphere

A. The Solution

Exposure of apatite to seawater at 1 atmosphere has been shown to cause dissolution of apatite within relatively short times and lead to an essentially stable concentration of ions in solution. Thermodynamic equilibrium exists only if the intensive properties of a substance are independent of time during the period allotted for experimentation and if no flux of matter or energy exists at the boundaries or in the interior of the substance (Kirkwood and Oppenheim, 1961). All reactions that affect the activities in solution must contribute to the final thermodynamic state of the solution. The heterogeneity of the reacting solid can cause many "side" reactions. These "side" reactions, as well as the dissolution of the apatite fractions, affect the activities of the ions in solution and thus the solubility product of the apatite. Consequently, the ability of the system to achieve the classical thermodynamic equilibrium described by Kirkwood and Oppenheim is strongly altered. Heterogeneity of a solid and the occurrence of a series of reactions proceeding simultaneously leads to the establishment of a "steady-state", where a flux of matter or energy at the boundaries of the substance exists (Wollast, 1974). The approach to classical thermodynamic equilibrium becomes very slow and asymptotic

in nature. In many situations a quasi-equilibrium is established or approached because of the formation of meta-stable intermediates, the formation of which kinetically hinders further approach to true equilibrium. Thus the observed effect in solution will be one of concentrations unchanging with time. It is these concentrations that have often been used by other workers to calculate solubility products, when in reality the values are only quasi-equilibrium concentrations.

Nancollas and Tomazic (1974) have concluded, "... a analysis of solid/solution experimental data solely on the basis of thermodynamic solubility products is an oversimplification. Kinetic considerations may be of paramount importance in controlling the formation of calcium phosphate phases during precipitation reactions". Although their conclusions were derived from crystal growth studies, the same conclusions certainly apply to interactions of apatites with seawater.

A.1. Unspiked Seawater

Comparison of the dissolution results of apatite in seawater with the dissolution results in NaCl solutions shows remarkably little difference. The common ion effect predicts, among other things, that a large concentration of a common ion, as is found in seawater, should reduce the solubility of

the solid significantly. This effect can be seen in the experiments in which a common ion was added to NaCl solutions. However, there are a number of mechanisms that can reduce the effective concentration (activity) of an ionic species, thereby promoting the dissolution of the solid. The most well-known of these in seawater is ion-pairing. Activities can also be affected by the way the ions interact with water. The solvation of ions involves the formation of water sheaths around the ion. Each type of ion has its own particular water sheath structure and so the effect of water and ion solvation is peculiar to each ion and ion-pair. This is further complicated in seawater by the extent of this water structuring.

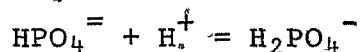
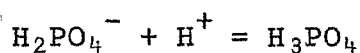
In the case of the component ions of apatite, significant amounts of the anions are ion-paired; while about 90% of the cations, calcium and magnesium, are free ions (Berner, 1971). Warner has suggested about 44-45% of the fluoride appears as MgF^+ , 2% as CaF^+ and the remainder, as free ion (seawater 30-32‰ salinity): The amount of HF at the pH of seawater is negligible. Thus the fluoride activity is about one-half the actual concentration.

Atlas (1975) has shown that essentially all of the phosphate is contained in ion-pairs. His values for the percentages of phosphate in various ion-pairs are given below.

% of Total Phosphate Species as Ion-Pairs

	PO_4^{-3}	HPO_4^{-2}	$\text{H}_2\text{PO}_4^{-}$
Ca	7.6	4.7	0.01
Mg	1.5	41.7	0.1
Na	0.01	15.	0.1
free	0.01	28.7	0.9

A second factor that could increase apatite solubility is the phosphoric acid dissociation system:

 k_1  k_2  k_3

A number of authors have reported values for the dissociation constants for phosphoric acid in seawater (Pytkowicz and Kester, 1968; Atlas, 1975), but these constants are only apparent constants, i.e., the calculations to produce the constants include both activities and measured concentrations. A difference in the constants can be found comparing dissociation in NaCl solutions to dissociation in seawater:

	pk_1	pk_2	pk_3	
NaCl Solution	1.72	6.40	11.2	(Atlas, 1975)
34.8 % SW	1.7	6.11	8.9	

Although the above figures indicate that most of the phosphate ions are present in ion-pairs, only values of the stability constants give an indication of the stability of the ion-pair. The table below gives literature values of relevant ion-pair stability constants.

Stability Constants of Relevant Ion-Pairs

	MPO_4	MHPO_4	MH_2PO_4	MF
Na	1.13(1)	4.79(1), 4(2)	14.0(1)	
Mg	9.29(1)	722(1)	2500(3), 7860(1)	19.3(4)
Ca	7.49(5) 5(6) 12(7), 25.6(8) 7.35(1)	590(5) 446(1) 380(9)	$2.9 \times 10^6(8)$ $2.24 \times 10^6(1)$	4.3(4)

- 1) Atlas (1975)
- 2) Smith and Alberty (1956)
- 3) Childs (1970)
- 4) Elgquist (1970)
- 5) Moreno et al. (1966)
- 6) Gregory et al. (1970)
- 7) Davies and Hoyle (1953)
- 8) Chughtai et al. (1968)
- 9) McDowell et al. (1970)

These values show that PO_4^{-3} in solution enters into stable ion-pairs, as well as the phosphoric acid system. The relatively high stability of the ion-pairs of the two main phosphate species (PO_4^{-3} , $\text{HPO}_4^{=}$) should have a profound effect on apatite dissolution. Much less ion-pairing occurs in NaCl solutions, compared to seawater.

A.II. Spiked Seawater

Experiments were conducted with seawater spiked to simulate interstitial waters that might be found in upwelling zones.

The phosphate concentrations required to reduce significantly the rates of dissolution that were reported by Dedhiya et al. (1973, 1974) ($10^{-3}M$) are greatly in excess of normal phosphate concentrations in seawater ($10^{-6}M$) and interstitial phosphate concentrations reported for upwelling zone sediments ($10^{-4}M$), Burnett, 1974). Gulbrandsen (1969) predicted that increased phosphate activities should decrease the solubility of apatite. However, the extensive ion-pairing of phosphate species in seawater suggests that very high concentrations of phosphate are required to reduce apatite dissolution in the oceans significantly.

Fluoride ions are not as completely ion-paired as phosphate ions and the reaction of fluoride with an apatite leads to the formation of a less-soluble fluoro-apatite. Thus a change in apatite dissolution should be apparent with a smaller increase in fluoride activity relative to the change in phosphate activities necessary to produce the same results.

Examination of the results of apatite exposure to seawater spiked to 5, 100 and 500 ppm NaF showed that fluoride concentrations of 10^2 to 10^3 times the fluoride concentration of

seawater were necessary to cause precipitation of a fluorapatite phase. At fluoride concentrations of less than 100 ppm there is probably an adsorption of fluoride on the apatite surface and subsequent alteration occurs to form fluorapatite. At concentrations above 100 ppm precipitation of fluorapatite and CaF_2 directly from solution likely occurs (McCann, 1968).

The formation of fluoro-phosphate ion-pairs has not been given much consideration by previous workers, although this would further tie up common ions and promote dissolution. However, Ingram (1968) and Simpson (1968, 1969) have suggested that the species FPO_3^- could form as some sort of intermediate on the apatite surface during reaction with a fluoride-containing solution.

Alteration of the Ca/Mg ratios can alter the dissolution process of apatite in two ways: (1) a change in the extent of ion-pairing and (2) alterations in the solid surface that would not occur with exposure to unaltered seawater. A decrease in magnesium would liberate some HPO_4^{2-} . The increased amount of phosphate would then depress the tendency for dissolution. Figure R57 shows that less phosphate went into solution in the Ca/Mg = 10 solution compared to the Ca/Mg = 2.5 solution. On the other hand, a decrease in the calcium concentration should have less effect than magnesium on ion-pairing. In Figure R55, we can see that there is a slight

decrease in dissolution for the reduced calcium solutions compared to dissolution in regular seawater.

7. Atlas (1975) reported virtually no change in TCO_2 in his experiments with alkalinity effects on apatite dissolution. This was similar to the results of this investigation. Because of the greater solubility of apatites with high carbonate content (LeGeros, 1967a, b), the stability of such an apatite that was formed on the original apatite surface would be low. As rapidly as this new apatite formed, it is dissolved back into solution. Thus the observed effect is one of essentially no change in TCO_2 .

At one atmosphere pressure, the effect of the solution environment on the dissolution process can be summarized in terms of ion-pairing. Processes which contribute to increased ion-pairing with ions common to those that make up apatite will increase the dissolution. Processes which decrease ion-pairing and liberate ions common to apatite will cause a decrease in dissolution.

A.III. Pretreated Surfaces

If the original surface of an apatite is altered when the apatite is exposed to solutions whose composition is unlike regular seawater, then the solubility behavior of this apatite in regular seawater should be different than the behavior of an unaltered apatite in regular seawater.

These differences in behavior are seen quite distinctly for the apatites tested. Examination of the results of repeated exposures to unspiked seawater showed a noticeable decrease in concentrations of the ions common to apatite released to solution with time. There was also a decrease in the length of time that elapsed before there was no apparent change in concentrations in solution. Exposure to seawater of phosphate-pretreated surfaces showed that if a phosphate-rich phase had been formed on the apatite surface, it was only loosely held, whereas the behavior of surfaces pretreated in fluoride-spiked seawater indicated the existence of a more complex assemblage of phases on the apatite surface that more effectively reduced the solubility of the apatite. Examination of the graphs for the fluoride-pretreated surfaces showed that a regime with no apparent change in concentration with time was rapidly achieved after the surface was exposed to unaltered seawater.

A.IV. Solubility Product Constants

A number of values for solubility product constants for apatites have been reported in the literature. The calculation of most of these values has been based on the knowledge of the solution activities at the time when equilibrium was assumed to have been reached and on the assumption that the chemical composition of the solid was adequately defined

and remained essentially unchanged throughout the reaction. Errors in either of these assumptions would certainly lead to significant errors in the calculated solubility product and these become especially important in the case of apatite because of its low solubility in water. Values for solubility products for hydroxyapatite in water have been reported in the range of 10^{-110} - 10^{-120} with constants for the less-soluble fluorapatite about 10^{-10} smaller.

The heterogeneity of natural apatites makes a statement of the real phase composition of the reacting surface difficult. Reactivity can thus only be determined by experimentation. Calculations of solubility products on the basis of thermodynamic information must be appropriate to the phase in question. As has been shown in this study, the reacting surface of an apatite is an assemblage of phases, the composition of which is a function of the physical and chemical environments, the characteristics of the apatite and of alteration as reaction proceeds. The ESCA and SEM results have shown that surface alteration does proceed as the reaction proceeds and we can no longer assume that the composition of the initial reacting surface remains essentially unaltered throughout the reaction.

The other assumption, that the final concentrations in solution represent equilibrium concentrations, is also invalid in this case. When a pure simple solid dissolves

in a pure liquid, the final solution concentrations do represent equilibrium concentrations and can be used to calculate the solubility product constant. However, with heterogeneous solids the presence of "foreign" phases and ions alters the chemical activities in both the solution and on the reacting surface. The presence of these "foreign" phases creates new rate-determining reactions which alter the rate of approach to the time until equilibrium has been reached. Thus the apparent effect is an equilibrium situation, whereas in reality a "quasi-stable" situation has developed, where alteration of concentrations does take place, very slowly in some cases because reactions with a common ion may be going in opposite directions relative to several phases.

In this study solubility product constants were not calculated for two reasons: (1) since natural phosphorites are heterogeneous solids, a chemical description of the bulk phase(s) does not adequately describe the composition of the reacting phase and (2) the interaction of the apatite with seawater leads to the alteration of this reacting surface and causes its composition to vary with time and to be a function of the surrounding environment.

As an example calculation, suppose we assume that the composition of Mexican apatite is that of pure fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Then we can calculate a solubility product constant, assuming that the solution concentrations are

equilibrium concentrations:

$$\begin{aligned}
 K_{sp} &= a_{ca}^{10} \times a_{po_4}^6 \times a_f^2 \\
 &= (6.8 \times 10^{-3} \times 0.26)^{10} \times (3.4 \times 10^{-4} \times 0.09 \times 0.033)^6 \times \\
 &\quad (11.5 \times 10^{-5} \times 0.63)^2 \\
 &= 1.66 \times 10^{-72}
 \end{aligned}$$

However the bulk chemical analysis has shown the Mexican apatite composition to be: $Ca_{8.5}(PO_4)_{5.1}(CO_3)_{0.27}F_{1.6}$

$$K_{sp} = 2.3 \times 10^{-62}$$

(Activity coefficients from Atlas (1975) and Berner (1971))
 The difference in these two numbers quickly show that unless the composition of each and every phase on the reacting surface is known and accounted for in the calculation, the value obtained for the solubility product is invalid. The ESCA and SEM results have also shown that even if the composition of the initial reacting surface was known, the calculation of a solubility product would still be wrong since alteration of the surface phase(s) occurs during the reaction.

The calculation of the thermodynamic solubility product is dependent on certain assumptions. The evidence from this study shows that these assumptions cannot be made in the case of the interaction of apatite with seawater. Similarly the calculation for the partial molal volume changes depends on the phase in question. Other thermodynamic calculations

which depend on these same assumptions are also invalid.

Thus, the fundamental question is: what are the reactants at any given time in this reaction? Once this is established, the thermodynamic information then available will become predictive.

A. V. Kinetics of Interaction

The rate of solid dissolution is a function of the surface area, a rate constant, and the solution concentrations at initial, intermediate, and equilibrium times. Garrels et al. (1961) and a number of other workers have suggested that concentration could be related to time by taking the time expression to the power $-1/2$, which would give a linear expression of the rate. Extrapolation of the slope to infinite time should then give a reasonable estimate of solubility. However, as recently noted by Plummer and MacKenzie (1974), the kinetic mechanisms of the surface reaction must not change during the reaction and the approach to equilibrium must be long for Garrels et al.'s expression to be true. Since changing surface reactions do play an important role in the apatite-seawater reaction, estimation of the solubility or the rate by this method is invalid.

Alteration of the surface phases during reaction is also likely to alter the total surface area. Many workers have used the BET gas adsorption method as an estimate of the

surface area, but this method has several drawbacks:

- (1) the measurement represents the area onto which gases will adsorb, but does not take into account the difference in behavior of liquids, (2) gas surface area will include adsorption onto non-apatite phases on the surface and (3) gas adsorption will occur much more readily on the surfaces within pores than will liquid adsorption. Thus surface area measurement by gas adsorption will be "high", and does not reflect alterations in the reactive surface area as reaction proceeds. Evidence for this alteration can be seen in the ESCA and SEM data.

Porosity plays an important role in the reactivity of phosphorites (Caro and Greeman, 1961). The "trapping" of liquid within pores of the solid during reaction can create specialized environments where new phases can be readily formed in comparison to the main exterior of the solid.

Examination of the concentration versus time curves of this study shows three regions. The first region shows a rapid change in solution concentrations with time. This represents the interaction of the original surface with the original solution. The second sector shows a decreasing rate of change in the solution concentrations, representing an alteration of the surface. The chemical

reactions of the solution with the altered surface are becoming the dominant rate-determining steps. The final sector shows no observable change in concentrations with time. It should be emphasized that the change is not "observable", although in reality changes are occurring.

This "stable" regime is different than would exist if the original reacting surface phase(s) had not been altered during the reaction. The regime that is achieved is highly dependent on the reaction environment because the phase(s) formed during alteration of the surface are themselves functions of the environment.

Like the calculation of the solubility product constant, the calculation of the rate constant depends on knowledge of the variables used in its calculation. And as for the solubility product, the rate constant can no longer be calculated by assuming no alteration in the reacting surface.

B. Solid

B.I. Mechanism of Surface Reactions

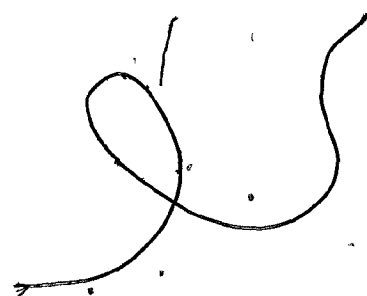
The term "surface phase" commonly used in discussion of

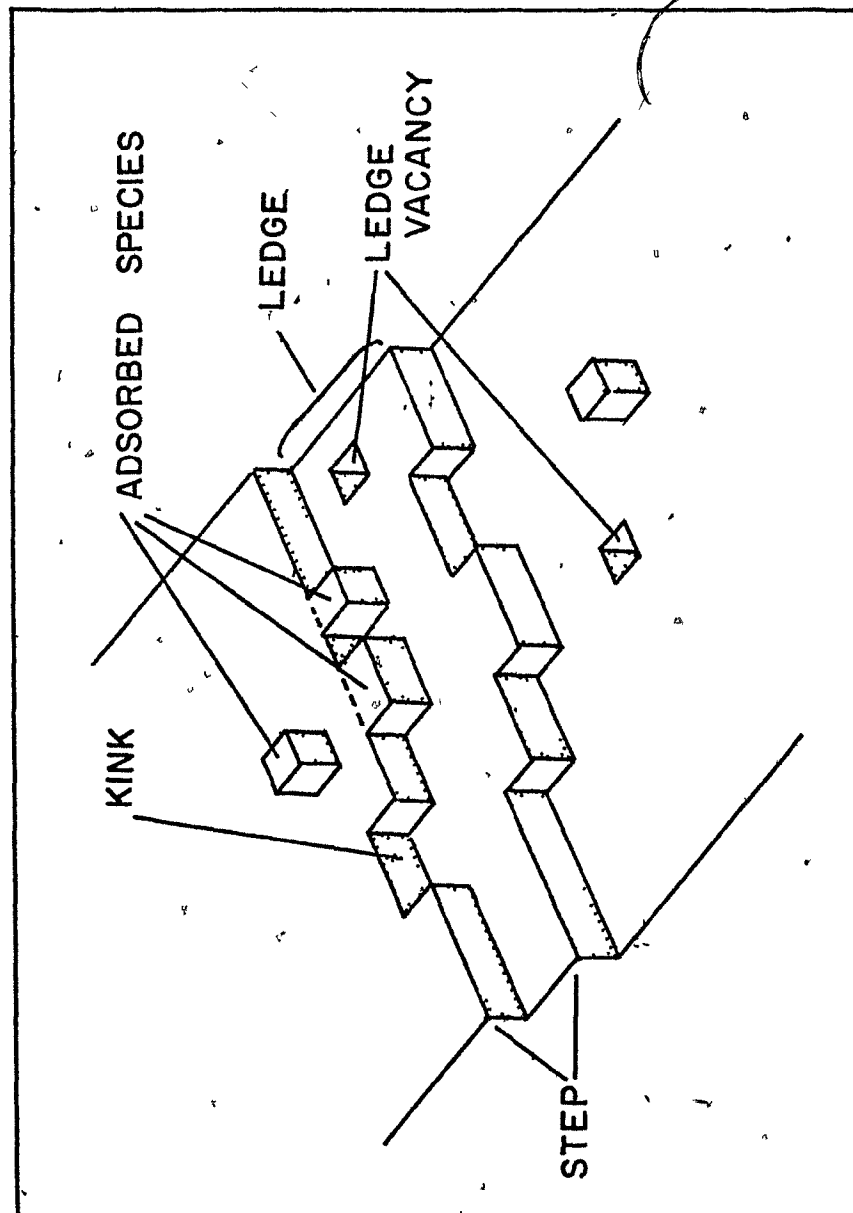
solid-solution interactions gives the impression that a total covering of the original surface of the solid takes place during the reaction. This is not likely to be the real case. It is better to describe the interaction of the solid with a solution in terms of the phases and ions adsorbed onto the solid surface. The real solid surface contains a wide variety of reactive sites. The reactivity of these sites is a function of a large number of factors which determine what phases or ions can occupy these sites. In some cases the occupation of a "defect" by an ion alters the reactive surface of the solid, but no new phase is created, nor does the ion appear "foreign" to the rest of the crystal.

The reactivity of sites can be due to chemical "defects" or to physical structures on the surface (Figure D1). The physical structures can be described as kinks, steps and ledges (Burton et al., 1951). For dissolution to proceed, free energy barriers must be overcome; once this is done, steps retreat, exposing a ledge. The presence of impurities in the apatite lattice can either inhibit or promote this retreat by their effect on the free energy barriers. Because of the nearness of crystal neighbours, occupation of a kink site by an adsorbing foreign ion seems to have the most effect on the dissolution process.

Adsorption at any one of the sites described above can inhibit dissolution in two ways: (1) certain active sites

Figure D1 : Schematic Diagram of a Solid Surface
Showing Steps, Kinks, and Ledges
(.from Davey, 1976)





may be necessary for the completion of chemical reactions and to catalyze chemical reactions and (2) a change in surface free energies may take place. Reduction of surface free energies by differing amounts, depending on the type of sites and the adsorbing ion, may cause alteration in surface structure and lead to the formation of either more or less soluble phases. Surface free energy differences can also promote surface diffusion-controlled recrystallization. Further, also the presence of impurities on certain crystal faces may promote or inhibit crystal growth in certain directions. For example, the presence of carbonate may restrict growth along the a-axis (LeGeros et al., 1967a).

Any of these sites are made up of groups of crystal unit cells. Each cell unit may contain a "defect" due to either mechanical alterations or an absence or addition of a component ion. These chemical defects alter the surface charge and provide a site within a crystal lattice for the adsorption of ions from solution. These defects in toto also affect the net surface free energy.

Surface charge is important from the point of view of the solution, since it can determine the ability of a surface to adsorb ions from solution. The surface charge of apatite is dependent on the pH and ionic strength of the solution. Bell et al. (1973) found that the replacement of surface OH^-

groups by F^- decreased the surface basicity because the fluoride had a weaker basicity and because the high electronegativity of the F^- decreased the basicity of other surface OH^- groups. Somasundaran and Agar (1972) found that the presence of PO_4^{3-} in solution made the apatite surface charge more negative, while at $pH > 7$ Ca^{+2} made the charge more positive. At low concentrations of F^- (at high pH) the effect on surface charge was similar to that of PO_4^{3-} , but of a smaller magnitude. At high F^- concentrations, the effect of charge was very hard to determine because of simultaneous chemical reactions, including adsorption and precipitation of fluoride-containing compounds. They did note that considerable periods of "aging" (time) were required before reasonably consistent results could be obtained. This would indicate that an alteration of the surface occurred during this "aging" and that they were actually measuring the surface charge effects of an altered surface. However, their results do show the net surface charge is an important factor in the reactivity of a surface.

B.II. Interaction with Unspiked Seawater

When the unreacted apatite is exposed to NaCl solutions the rate of reaction is controlled by the diffusion of ions through the liquid. There is much less ion-pairing in the NaCl solutions and probably little alteration of the original

surface of the solid. Exposure of the surface to the solution probably removes disorganized loosely-held material, leaving behind a more insoluble and better-crystallized surface. Phosphoric acid dissociation would exhibit some control over dissolution, but in these experiments the pH and ionic strength were adjusted so that they were similar to seawater and thus the concentrations of the phosphate species would be approximately similar.

On the other hand, when the surface was exposed to seawater, ion-pairing played a significant role in dissolution and other species were present in solution to interact with the surface of the solid to form new phases. These new phases then exerted partial control over subsequent interactions with the solution until no further apparent changes of concentrations with time occurred. Alteration of the solution composition then must cause an alteration in the composition of the available phases. The rate of change of the surface is dependent on the ionic activities in solution, the stability and degree of ion-pairing and the thermodynamic stability of the surface in the newly altered solution.

B.III. Interaction with Spiked Seawater

Davey (1976) has suggested that differences in the characteristics of impurities (e.g., size, charge) cause them to interfere in the dissolution process in different ways.

Inhibition by fluoride may occur best at kink sites, whereas inhibition by organic molecules may occur best at ledge sites.

In the case of apatites, magnesium can substitute for calcium and fluoride for hydroxyl quite easily, and these two species can be expected to affect dissolution the most. The addition of carbonate to the apatite lattice introduces weak bonds which make the solid more susceptible to dissolution (LeGeros et al., 1967a). Addition of other calcium or phosphate ions to the apatite lattice can either complete an incomplete crystal thereby strengthening the solid and inhibiting dissolution, or they can form metastable compounds which may promote dissolution.

Electron micrographs of surfaces exposed to fluoride-spiked seawater showed the formation of CaF_2 -like crystals over parts of apatite crystals. It should be emphasized that these CaF_2 -like crystals do not form a complete covering over the surface, but are located at certain reactive sites and appear to inhibit dissolution by "protecting" crystal faces which are susceptible to dissolution.

In the fluoride-spiked solutions of low F^- concentrations, CaF_2 is not likely to form, but fluoride-hydroxyl exchange or fluoride adsorption may occur and lead to the formation of fluorapatite (Higuchi et al., 1969). As the fluoride activity in the solution is increased, the solubility product of CaF_2 is reached and surpassed, leading to

the formation at the solid-solution interface of a solution regime of supersaturated CaF_2 and the formation of CaF_2 on the solid surface (Farr and Elmore, 1962; Liang, 1971).

ESCA analyses of the surfaces exposed to seawater spiked with high fluoride concentrations indicated the increased concentration of fluoride in at least the top 10 atomic layers ($\sim 50\text{\AA}$) and a change in the speciation of calcium. This speciation change indicates a change in calcium bonding in the surface layer and thus the presence of a new phase (probably CaF_2).

Because of the interest in tooth decay (hydroxyapatite dissolution) many investigations of fluoride-apatite interactions have been made. Little attention has been paid to phosphate interactions; Dedhiya et al. (1973) noted that the presence of phosphate reduced the rate of dissolution of hydroxyapatite. Synergistic effects could be seen in strontium-phosphate spiked solutions, with a considerable decrease in the rate of dissolution, but no discussion of the phosphate interactions or mechanisms at the solid surface was made. Atlas (1975) has suggested that $\text{HPO}_4^{=}$ is the main phosphate species on the apatite surface that has been exposed to seawater, although this may hold true only for low solid/solution ratios. The additional phosphate in solution due to spiking may lead to the formation of other calcium

phosphates, such as monetite or brushite, although both of these compounds are more soluble than apatite in the pH = 8 region (Moreno et al., 1966; Brown, 1973). At the low phosphate concentrations found in natural waters or even the higher concentrations found in interstitial waters of upwelling zones, the ambient phosphate concentrations would probable have little effect on apatite dissolution.

Electron micrographs of the Ontario apatite surfaces exposed to seawater and to seawater with altered Ca/Mg ratios showed essentially the same morphological features. Rowles (1967) has suggested that as the Ca/Mg ratio is decreased (even in the pH = 8 region), whitlockite, $(\text{CaMg})_3(\text{PO}_4)_2$, is the most likely solid phase to form. If whitlockite does not form, a calcium-magnesium exchange might take place, leading to the formation of a more soluble magnesium-containing apatite. This phase would then rapidly re-dissolve.

Interaction with solutions of adjusted TCO_2 showed little variation in solution composition. High carbonate content might lead to the formation of a carbonate-containing phase at the apatite surface, with variation in crystal morphology, from the needle-shaped non-carbonate apatite to a calcite-like structure with a carbonate content of the apatite of greater than 20% (LeGeros, 1967 a,b). LeGeros et al. (1967a) have suggested that the presence of carbonate bonds weakens the apatite lattice, making it more susceptible to dissolution.

B.IV. Pretreatment of Surfaces

Examination of pretreated apatite surfaces before and after exposure to regular seawater showed that the surface altered by exposure to the initial solution was further altered in response to the change in the solution. Electron micrographs of surfaces pretreated in fluoride-spiked seawater showed the formation of CaF_2 -like crystals. Subsequent exposure to regular seawater removed most of these crystals. Either some of the originally-deposited crystals dissolved because of exposure to a solution of low fluoride activity or all of the originally-deposited crystals were dissolved creating a supersaturation of CaF_2 and the reformation of CaF_2 crystals.

Apatite surfaces that were repeatedly exposed to unaltered seawater showed a "weathering" effect at the end of the first period of exposure that was further developed by subsequent exposures to seawater. Because of the complexity of the solid used, incongruent dissolution of the apatite was the most likely process. This could be due to the wide variation in ionic activities across the apatite surface, caused by crystal defects, degrees of crystallinity, and the presence of several phases.

II. Interactions of Elevated Pressures

A. The Solution

A.I. NaCl Solutions and Unspiked Seawater

Increased pressure caused an increase in dissolution of the apatites in NaCl, unspiked seawater, and fluoride-spiked seawater solutions, where dissolution was defined to occur when an increase in ionic concentrations in solution was observed.

Increased dissolution with increased pressure can be attributed to pressure effects on the phosphoric acid system, the formation of ion-pairs and the dissolution process.

Ion-pairing and the phosphoric acid system play a large role in seawater; in NaCl solutions ion-pairing has much less effect and the acid system would then dominate the solution effects. Hamann (1972) has reported $K_{1000\text{bar}}/K_{1\text{bar}}$ (25°C) for the first and second dissociation constants of 1.93 and 2.64 respectively. Increased pressure increases the dissociation of the acid. The increased PO_4^{3-} should inhibit the dissolution process at elevated pressures compared to the dissolution process at 1 atm.

Increased pressure should increase the dissociation of ion-pairs. This would also inhibit the dissolution process, especially in seawater.

If the partial molal volume change representing the dissolution reaction in water were favourable (i.e., promoted dissolution), then a pressure increase should further promote dissolution. Integration of Planck's equation:

$$\partial/\partial P (\ln K) = - \Delta V/RT \quad (1)$$

in terms of pressure yields:

$$\ln(K_p/K_{1\text{bar}}) = - \Delta V \cdot P/RT + (P^2/2RT) (\Delta k) - (P^3/6RT) (\Delta \lambda) \quad (2)$$

where Δk is the compressibility constant and $\Delta \lambda = \partial/\partial P (\Delta k)$.

The assumption can be made at pressures less than 1000 bar that:

$$\Delta k \approx \Delta \lambda \approx 0 \quad \text{or} \quad \ln(K_p/K_{1\text{bar}}) = -P/RT (\Delta V) \quad (3)$$

However, the assumption that the compressibility factor is not a function of pressure is invalid and Hamann (1973) has suggested the expression:

$$RT \ln (K_p/K_{1\text{bar}}) = - \Delta V (P/RT + bP) \quad (4)$$

where b has the generalized value, $9.20 \times 10^{-5} \text{ bar}^{-1}$.

The partial molal volume change due to dissolution is represented by the value of the sum of the partial molar volumes for the products minus the partial molal volumes for the reactants. If we assume that the compound, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$

dissolves in water, then we can calculate the partial molal volume change using data from Millero's compilation (1972 a,b) and density data from Fisher (1973). (25°C, 1 atm.)

$$V = V_{\text{prod}} - V_{\text{react}} = -158.9 - 425 = -583.9 \text{ cc/mole}$$

Although these values represent dissolution in water at 1 atm., results for seawater would not be much different. The value indicates that dissolution should be strongly pressure dependent, which is confirmed by the results from this study of dissolution (expressed in terms of the solution). However, the effect of pressure does not appear to be as strong as the calculations would predict. The calculation is dependent on the phase(s) assumed to be dissolving. Increased pressure would also promote the rate of alteration of the surface. Thus the observed effect in solution is a combination of pressure-induced dissolution and modification of this dissolution by alteration of the surface.

For dissolution to proceed, surface free energy barriers must be overcome. The application of pressure to the apatite-seawater system provides energy necessary to overcome these free energy barriers. The introduction of a known inhibiting ion to the solution assisted in the alteration of the original surface and new and higher free energy barriers to dissolution were constructed. The increase in temperature provides the energy necessary for the alteration of the original surface layer to a less-soluble form. This alteration of the surface must have an energy barrier lower than the energy barrier against dissolution.

Thus classical thermodynamic considerations fail in predicting no dissolution with pressure. In complex systems, such as apatite-seawater, reactions at the solid-solution interface and the ability to overcome free energy barriers associated with these reactions dominate the dissolution processes and determine the rate and extent of dissolution.

A.II. Fluoride-Spiked Seawater

The addition of fluoride to seawater reacting with the Marine apatite further reduced the pressure-induced dissolution relative to the extent of dissolution seen in unspiked seawater. Fluoride concentrations in the solution effluent were considerably reduced due to uptake by the solid. The increase in pressure simultaneously promoted dissolution of the solid and the fluoridation of the apatite. A balance between chemical reactions promoting the stabilization of the solid exposed to the solution and the achievement of the greatest volume decrease with pressure increase must be achieved.

B. The Solid

B.I. Interaction with NaCl Solutions and Unspiked Seawater

Increased pressure promoted dissolution of the solid. As the pressure increased some of the apatite dissolved, altering the surface of the solid until after some time a

stable surface was obtained and there was no apparent change in concentrations in solution with time. A further increase in pressure promotes more dissolution by altering the chemical environment and reaction rates until a new stable surface is obtained and there is again no apparent change in solution concentrations with time.

The dissolution in NaCl solutions was essentially a process with few complications. Reasonably linear relationships of concentrations in solution to pressure were obtained.

ESCA and electron micrographs of apatite surfaces exposed to seawater showed that a more complex system was in control in this case. The formation of the rod-like crystals and the uptake of silicon by the Mexican apatite are evidence for a significantly altered surface and for the formation of new phases at certain sites on the apatite surface. The concentrations of the relevant ions monitored in the effluent solutions showed reasonably linear relationships with pressure. It is possible that dissolution of apatite occurs as pressure is increased, followed by alteration of the surface to reflect the change in the physical and chemical environment. The altered surface does not have to contain a pure apatite phase but is likely to contain several phases of varying composition. Considering the complexity and heterogeneity of the samples used in this study, a complex assemblage of phases is probably created on the apatite surface in nature. As the pressure is altered, conditions in the solution are

altered and the phase composition, number of phases, and the extent of coverage of any one phase on the surface are altered. This change can be seen when the ESCA results of the Mexican apatites exposed to seawater at 125 atm. and 1000 atm. are compared. Also, electron micrographs of the 1000 atm. surface showed a more extensive coverage of the rod-shaped crystals. The crystals on the 125 atm. surface were fewer in number, but longer in length.

B.II. Interaction with Fluoride-Spiked Seawater

The inhibiting effect of large concentrations of fluoride on dissolution processes in the solution is also found after examination of the solid. Although ESCA results were somewhat the same for surfaces exposed to regular seawater, less uptake of silicon or actual loss of aluminum were seen. Examination of the results of the Mexican apatite surface exposed at 125 atm. showed more inhibition effect than the surface exposed at 1000 atm. Evidently some of the inhibiting effects of the fluoride were overcome by the increased pressure. Electron micrographs of the surfaces showed many fewer and generally smaller rod-like crystals on the fluoridated surfaces. The adsorption of fluoride or fluoride-containing phases seems to prevent silica adsorption by occupying surface sites. The presence of more rod-like crystals on the surface exposed to fluoride-spiked seawater at 1000 atm. compared to the 125

atm. surface indicates that the increased pressure is keeping the fluoride in solution and thus keeping free certain surface sites for the deposition of the rod-like crystals.

MacDonald and North (1974) predicted increased solubility with increased pressure for CaF_2 in water. Inhibition of the dissolution process by the easily formed CaF_2 may be limited by the increased pressure-induced dissolution of CaF_2 . Thus fluoridation of the apatite surface may proceed via the formation of other, more complicated, fluoride phases. At high pressures, the rates of formation and the stability of these species may be the determinants of the fluoride inhibition of apatite dissolution.

C. Temperature-Pressure Effects

The one experiment with two different temperatures and increasing pressure showed that physical as well as chemical effects could negate or reduce the pressure effect. In both cases of temperature, the increasing pressure increased apatite dissolution, although the higher temperature caused less dissolution than the lower temperature.

Although pressure is an important, but often neglected, thermodynamic consideration in the ocean, the results in this study indicate that physico-chemical effects are important in the deep-sea dissolution of apatites. In some circumstances the chemical environment may so alter the reacting-surface

of the apatite, as to negate completely the pressure-induced dissolution effect, whereas in other cases, the environmental alterations may be synergistic and lead to greater dissolution than would otherwise be predicted.

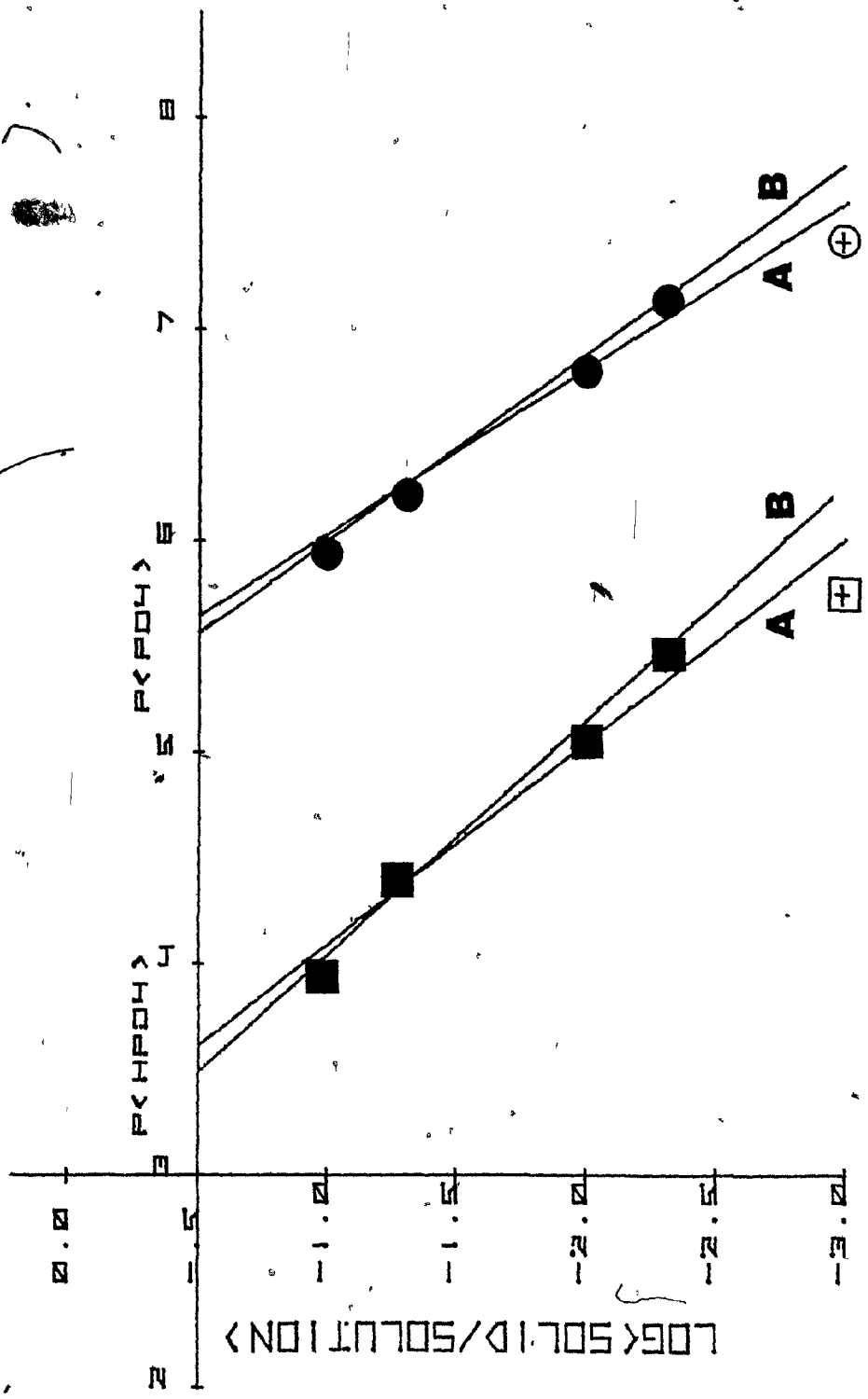
D. Surface Problems

D.I. Variation in Surface Area

Atlas (1975) has suggested that when apatite is reacted with seawater an altered surface is formed, with $\text{HPO}_4^{=}$ as the main component species. He based his prediction on the fact that he obtained a linear relationship of $p(\text{HPO}_4^{=})$ in solution to the log (solid/solution) ratio, but a more complex relationship for $p(\text{PO}_4^{-3})$ to the ratio. His solid/solution ratios were 0.01, 0.05, 0.25, 0.5, and 1 g/100 cc. A similar plot was constructed for the data of this study (Figure D2), with solid/solution ratios of 0.1, 0.5, 1, 5, and 10 g/100 cc. The log of the concentrations of both phosphate species showed a linear relationship to the log (solid/solution) ratio. However, a better fit to the data for the $\text{HPO}_4^{=}$ was obtained with a parabolic relationship. In both cases a better linear fit was obtained by eliminating the 0.1 g/100 cc point. Examination of Atlas' data shows that a linear fit was possible through the data points representing the three largest weights of solid for both the $\text{HPO}_4^{=}$ and the PO_4^{-3} cases. This would indicate that a different mechanism for the seawater-apatite reaction is occurring at low solid/solution ratios compared to

Figure D2 : $p(\text{HPO}_4^=)$ or $p(\text{PO}_4^{-3})$ versus \log
(solid/solution)

■+⊕ Line A ($\text{HPO}_4^=$)	$r^2 = .974$
■ Line B ($\text{HPO}_4^=$)	$r^2 = .995$
●+⊕ Line A (PO_4^{-3})	$r^2 = .976$
● Line B (PO_4^{-3})	$r^2 = .998$



mechanisms occurring at high solid/solution ratios.

Weir et al. (1971) obtained essentially the same solubility constants for hydroxyapatite in water using 0.1, 0.5, 1, and 10 g/100 cc. However, they did note that although the 0.1 g/100 cc sample gave the same solubility constant as the other samples at high pH, at low pH the results for this solution gave a lower solubility than predicted from the high pH results. At low solid/solution ratios, solution processes probably dominate the dissolution mechanisms, whereas at high solid/solution ratios, processes on the solid surface become more important. If processes in solution dominate the dissolution mechanisms, then in seawater, $\text{HPO}_4^{=}$ would be expected to be the dominant phosphate species. If solid surface processes dominate the dissolution mechanisms, then the original apatite species, PO_4^{-3} , would be more important.

D.II. Mechanical Handling

The general result of grinding is to create a more reactive solid by an increase in surface area. However, surface properties can be altered (Gregg, 1968), including possible phase transformations (Gammage and Gleason, 1976). Gregg (1968) suggested that milling may cause a destruction of pores in the solid, leading to a decrease in the effective surface area. Examination of the results of varying particle sizes in this study show in general only a slight increase in dissolution (where the increase was measured by the increase in

solution ionic concentrations) with increased grinding. Although phase transformations are unlikely, the small differences in dissolution of the two grinds could indicate that pore destruction occurred because of grinding. And although surface measurements by gas adsorption may give a value for the total surface area, they do not identify the degree of reactivity of the various sites nor the effect of porosity on the dissolution (probably highest for Marine apatite, lowest for the Ontario and Quebec apatites), nor do they make corrections for gas adsorption by non-apatitic members of the rock sample. Hill et al. (1954) found that the reproducibility of grindings was very difficult to obtain and that grinding had a strong effect on the reactivity of the apatite. They found that the surfaces of fine-grained apatites showed a slight and linear decrease in increase in particle size from 10-400 mesh. The high surface areas of coarse-grained apatites were rapidly reduced in going from 10-50 mesh particles. Further reductions in mesh size gave essentially no change in surface area.

In the natural environment, pore water composition and the reactions within individual grain pores may be the most important determinants of the reactivity and dissolution behavior of apatites (Caro and Freeman, 1961). Only in this restricted environment can conditions exist where apatite dissolution and precipitation can occur.

CONCLUSIONS

The objective of this study was to determine if exposure of apatite to seawater caused an alteration of the apatite surface and how this altered surface affected the diagenetic reactions of marine apatite. The results of the study show that alteration of the surface did take place. The formation of and composition of this altered surface were found to be functions of the physical and chemical environments and the characteristics of the original apatite surface.

On the basis of the phase rule when $F = 0$, $P = C+2$ ($2 = \text{temperature} + \text{pressure}$) and if temperature and pressure are fixed, then an alteration in the number of components must cause an alteration in the number of phases. This alteration is readily seen in examination of the photomicrographs of the apatite surfaces exposed to fluoride-spiked seawater. The phrase, "altered surface phase" implies to most readers that a complete covering of the original surface has taken place. However, the photomicrographs have shown that the location of the new phases is a selective process. Although the original surface may be totally covered by new phases, this layer is most likely to be a mosaic of phases. The formation of each new phase is dependent upon the reactivity of the original surface at each site. The reactivity can be defined in the chemical sense by the free energy barriers to chemical reactions that are able to alter the original characteristics of these sites;

in the physical sense, the reactivity is defined by the physical characteristics of the site (e.g., pore construction, location of nearest neighbouring crystals, placement of new phases).

Thermodynamic variables which are said to be inhibiting dissolution are those variables which increase free energy barriers to dissolution reactions and promote the rates of chemical reactions other than dissolution. Variables that promote dissolution are those that promote the construction of lower energy barriers and/or inhibit rates of chemical reactions other than dissolution.

Comparison of the results from this study of dissolution in NaCl and seawater solutions showed that there were much smaller differences in the ionic concentration increases (due to dissolution) than could be predicted from common ion theory. These differences were due mainly to the high degree of ion-pairing of the component anions of apatite in seawater. Ion-pairing in seawater creates the chemical environment that promotes apatite dissolution in the present open oceans. Thus the open ocean cannot be considered saturated with respect to apatite. This agrees with the suggestion of Skopintsev (1972) that the oceans are only 50-70% saturated with respect to apatite. The preservation of apatite material from biological sources (teeth, bones etc.) is probably due to organic coatings on the material.

This study has shown that elevated pressures and/or low temperatures promote apatite dissolution, by not promoting the formation of phases on the surface of the apatite which can "protect" the apatite from dissolution. However, the results from this study provide evidence to show that the "proper" chemical environment can successfully inhibit dissolution and permit the growth of apatite deposits, thereby negating dissolution tendencies caused by the deep-sea physical environment.

This "proper" chemical environment requires significantly

different ionic activities than found in typical open ocean seawater. Increases to about 10 ppm fluoride (from ~ 2 ppm in open ocean seawater) or to 10^{-3} M phosphate (from ~ 10^{-6} M in open ocean seawater) were found to be necessary to inhibit dissolution. A decrease in calcium activity promoted dissolution. Much less of a change in magnesium, compared to calcium, was necessary to affect dissolution. The presence of fluoride ion in seawater appears to be the best inhibitor of apatite dissolution in seawater. Apatite formation is likely to occur only in specialized chemical environment combined with the high surface area of sediments that offer the right kind of nucleating surface permit the creation of the "proper" chemical environment for apatite formation. Once deposits have formed, they are "preserved" by the alteration of their surfaces to the least-soluble phases.

Suggestions for Future Research

The most obvious avenue of future research is a more detailed investigation of the apatite surface before and after exposure to seawater. The reactivity of the surface has been defined as the sum of the reactivities of the individual "sites" on the apatite surface. A quantification of this "reactivity" and an in-depth examination of the mechanisms which regulate the alteration of the original surface layer would lead to a better description of the dissolution and formation processes. A scanning auger microprobe should be able to define chemically the pre-exposed surface and this evidence coupled with determinations of surface areas and porosity could lead to a reasonable estimate of the reactivity of the surface. The scanning auger microprobe could also be used to follow the changes that occur on the apatite surface as the reaction with seawater progresses.

Apatites are considered excellent "concentrators" of trace metals in the marine environment. This ability is probably related to the reactivity of the solid surface and the alteration that occurs with exposure to seawater. A complete description of the altering and altered surfaces would assist in the estimation of the trace metal geochemical cycles in the oceans.

Unfortunately little attention has been paid in oceanography to pressure as a thermodynamic variable. A determination of the effects of pressure on the phosphoric acid dissociation constants and the stability of ion-pairs in seawater could be combined with the experimental data from this study to give a complete description of the pressure-induced dissolution of apatite.

This study has emphasized the investigation of inorganic reactions and their effect on the alteration of the apatite surface. The effects of a reducing environment and pore waters containing a high concentration of organic compounds, which are typical of interstitial pore waters of upwelling zones, where most phosphorite deposits are found, have not been investigated in this study. A more complete simulation of typical pore water environments would give a more complete explanation of why apatites exist in the present oceanic sediments.

PHOSPHATES IN THE MARINE ENVIRONMENT

I. Formation

Marine phosphorites were first reported by the "Challenger Expedition" (Murray and Renard, 1889, 1891). Since then many reports have appeared in the literature. Recent reviews have been published by Bushinskii (1966), McKelvey (1967) and Tooms et al. (1969).

Phosphorite deposits generally occur in areas that can be best described as of shallow depth (less than 1000m), having a continuous supply of phosphate and having low active sedimentation. A map of the major phosphorite deposits is given in Figure P-1.

The loss of phosphate from the euphotic layer to the sediments and its subsequent mineralization is an important segment in the phosphate cycle in the oceans. Phosphorite formation has been suggested to be due to various mechanisms:

(1) direct inorganic precipitation (Kazakov, 1937), (2) phosphatization of existing sediments (Leckie and Stumm, 1970; Cook, 1972; Nriagu, 1976), and (3) decomposition of organic remains. The latter process could contribute in two ways: (a) accumulation of skeletal and tooth material and some shells (for example, the shell of the Brachiopod *Lingula* (McConnell, 1963), and (b) release of quantities of phosphate to the interstitial waters.

Close examination of each of these mechanisms will show that each mechanism cannot exist on its own, but

Figure P1 : Map of the world showing major upwelling zones and phosphorite deposits (after McKelvey 1966)

::: upwelling areas

xxx areas of major animal extinctions, red tides, etc.

- - major phosphorite deposits:

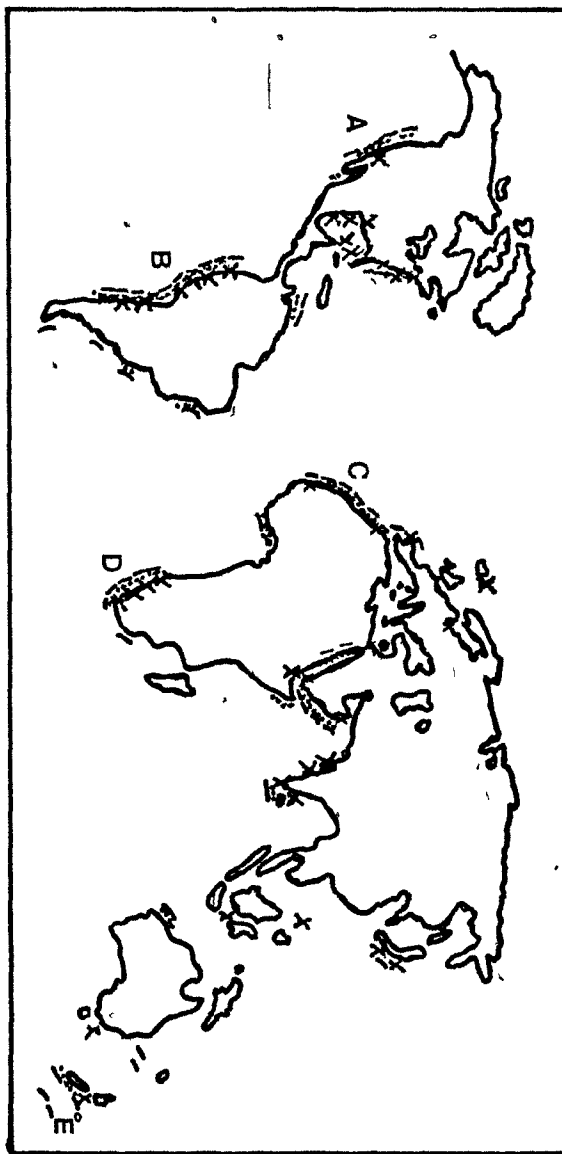
A California (d'Anglejan, 1967)

B Peru-Chile (Burnett, 1974)

C North-West Africa (Tooms et al, 1971)

D South-West Africa (Baturin et al, 1974)

E Pacific seamounts (Summerhayes, 1967)



rather phosphorite formation requires a combination of the three mechanisms and a specialized environment that does not "remove" or "overwhelm" the recently formed apatite.

Early classical thermodynamic calculations attempted to show that the oceans were saturated with respect to various forms of apatite (Kramer, 1964; Pytkowicz and Kester, 1967). However, various chemical interactions affecting the activities of the relevant species were not taken into account. As Skopintsev (1973) has noted, ion-pairing by phosphate species probably means that the oceans are only about 70% saturated with respect to apatite. Thus direct precipitation is only likely to occur in specialized environments where the ionic activities of the relevant species are raised above their normal levels in the open ocean.

Although direct precipitation may be possible, crystal theory demands a certain type of surface that is suitable for crystal nucleation and growth. Leckie (1969) and Leckie and Stumm (1970) have shown that calcite acts both as an excellent surface for the nucleation and growth of apatite and as an adsorbing surface for phosphate ions. These adsorbed ions can then interact with the calcite to form apatite, and this mechanism is probably responsible for the formation of apatite on Pacific Ocean guyots (Summerhayes, 1967; Slater and Goodwin, 1973).

Calcite is not the only material that is often associated with apatites. Nriagu (1976) and Cook (1972) have shown that phosphatization of clays can lead to the formation of apatite. Burnett (1974) has also observed freshly formed apatite crystals on diatom tests from the Peruvian upwelling zone sediments. Phosphatization of sediments, like direct precipitation, requires a specialized environment: continuous input of phosphate and an environment that does not remove the apatite as fast as it is formed.

The decomposition of organic material in the sediments could promote both of the above mechanisms. The release of quantities of phosphate to interstitial waters creates a continuous input of phosphate necessary for phosphatization of the sediments and increases the activity of phosphate perhaps leading to inorganic saturation and precipitation. The accumulation of skeletal and tooth material that is already apatite will naturally provide an excellent nucleating site for apatite crystal development. Although many areas of the present oceans may contribute large quantities of material to the sediments, they do not have the proper chemical and physical environment suitable for apatite formation. The present upwelling zones along the western coasts of the continents appear to offer the best environments for the formation of apatites in the present oceans.

There is a large quantity of organic material descending to the sediments, the oxygen minimum and the sediments coincide at a reasonable depth (Burnett and Chave (in prep.) (thus there is not much adsorption of phosphate by iron in the sediments) and there is low input of terrigenous material from the nearby land.

The formation of phosphorite may occur in the present sediments, but a specialized environment in the sediments is required, both for the formation of the phosphorite, and its preservation. Until the recent reports of Baturin et. (1972) and Veeh et al. (1973), phosphorite deposits were reported as being geologically old (Emery, 1960; d'Anglejan, 1967; Kolodny and Kaplan, 1970) and that phosphorite formation was not likely to occur in the present oceans. The size and age of the large deposits of phosphorite indicate that the conditions suitable for phosphorite formation must have been much more prevalent in previous geological periods than they are now.

Piper and Codespoti (1975) attempted to relate the age of phosphorite formations with periods of increased animal mortality in the oceans, which they speculated were due to alterations in the nitrogen cycle. Burnett (1974) has suggested that changes in sea level and ocean surface temperatures correlate well with the ages of major phosphorite deposits. The higher temperatures and decreased sea

levels (compared to modern) would create more of the shallow, warm water areas that promote higher productivity and thus more input of decomposing material to the sediments. These conditions would also provide the physical environment appropriate to phosphorite formation (Pevear, 1967). The results of this study show that cold and/or deep waters promote the dissolution of phosphorite. High volcanic activity during previous geological periods would increase the input of fluoride to the oceans which would promote the stability of apatites.

As the sea level rose, temperatures decreased and volcanic activity subsided, the size of areas best suited to phosphorite formation decreased. At the present time, except for phosphatization of existing sediments of calcite, phosphorite formation is only likely to occur in the sediments of upwelling zones off the western coasts of the continents. Small segments of these sediments most closely resemble the conditions that have existed at various times throughout geological history.

II. Diagenesis and Surface Alterations

The concept of a "protective" phases(s) preventing further reaction of a mineral phase with seawater has important consequences in sedimentary diagenesis and the recycling of phosphate in the oceans. "Inhibiting ions", such as fluoride

with apatites, affect seawater interaction with such minerals as calcite (affected by phosphate) (Berner and Morse, 1974) and silicates (affected by aluminum) (Willey, 1975, a,b).

Diagenesis can be affected in two ways: (a) the concentration of an ion required to effectively inhibit dissolution will be much less if alteration of only the surface phases can significantly reduce dissolution and (2) the formation of a "protective layer" can greatly inhibit further seawater interaction with the remainder of the mineral. Thus within the sediments large amounts of material are virtually unaffected by seawater and thus are restricted from being cycled back into seawater.

As phosphate is liberated by the decomposition of organic remains in the sediments and is subsequently mineralized, the formation of less-soluble phases on the surface of the minerals prevents the re-cycling of the phosphate into the nutrient cycle. Only significant changes in the physical and chemical environment which can alter this "protective layer" can alter the phosphate geochemical cycle. In the present sedimentary regime, conditions are such that the formation of a "protective layer" on newly formed apatite is more difficult.

The formation of various phases on the surface of apatite may also be the source of the ability of apatite to

concentrate uranium and other trace metals from seawater. ESCA results of surfaces exposed to seawater in this study showed that the surface layer could contain elements within phases that were very different from calcium phosphates. Similarly, the formation of phases on the surfaces of other minerals may be the controlling mechanism for trace metal residence times in the oceans. For example, the formation of manganese nodules and the ability of these nodules to also concentrate trace metals from seawater is probably related to the formation and alteration of the phases on the surfaces of the nodules.

Obviously, a more detailed investigation into the formation of surface phases on sedimentary materials and the ability of surfaces to exert chemical control over solutions which they are in contact should form an important part of discussions of marine geochemical cycles.

SUMMARY

- 1) The interaction of seawater leads to the alteration of the surface of the apatite. The composition of this altered surface is a function of the physical and chemical environment and the characteristics of the apatite. The altered surface, which may contain phases different from the phase that composes the bulk of the solid, then controls the kinetics of subsequent reactions.
- 2) The composition of the altered surface should not be described as simply a less-soluble form of apatite, but may involve a complex assemblage of phases.
- 3) The dissolution of apatite in seawater and NaCl solutions is a linear function of pressure over the range 30-1000 atm. and 5°C, where dissolution is measured by the change in concentrations of the relevant ions in solution.
- 4) The extent of pressure-induced dissolution can be modified by other thermodynamic processes which can inhibit dissolution.
- 5) The presence of fluoride in solution inhibits the dissolution of apatite, although fluoride concentrations greatly in excess of normal seawater are necessary. The high levels of fluoride permit the formation of compounds as CaF_2 on the surface, as well as fluorapatite.

6) Reduction in the activity of magnesium in solution reduces the dissolution tendency of apatite. Reduction in the activity of calcium increases the dissolution tendency of apatite, although a greater change in calcium, compared to magnesium, activity is necessary.

7) Although an increase in phosphate decreases the dissolution tendency of apatite, concentration levels in excess of upwelling zone pore waters are required.

8) The dissolution of apatites is an inverse function of temperature. Increased temperature promotes the rate of alteration of the surface and reflects the presence of energy barriers that must be overcome before surface alteration proceeds.

9) The ability of apatites to exist in oceanic sediments is a result of the alteration of the surfaces to more insoluble phases which inhibit the kinetics of dissolution. The problem of apatite dissolution in seawater must be described in kinetic terms, as well as in correct thermodynamic solubility calculations.

10) Description of marine geochemical cycles based on knowledge of bulk analyses of solids and solutions may be totally wrong. The error is caused by not considering the micro-scale chemical processes leading to the alteration of the reactive surface of a solid and the processes affecting the activity of relevant ions in solution.

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Addendum:

- Petrovic, R., 1976. Rate Control in Feldspar Dissolution -II. The Protective Effect of Precipitates. *Geochimica et Cosmochimica Acta*, 40, 1509-1522.

APPENDIX A: Characterization of Apatite Samples

Al

Figure A 1

Photograph of Apatite Samples

- A. Mexican (Banded)
- B. Ontario Brown (Wilberforce)
- C. Florida Pebble Collophane
- D. Marine Phosphorite
- E. Quebec-Ontario Blue-Green Massive

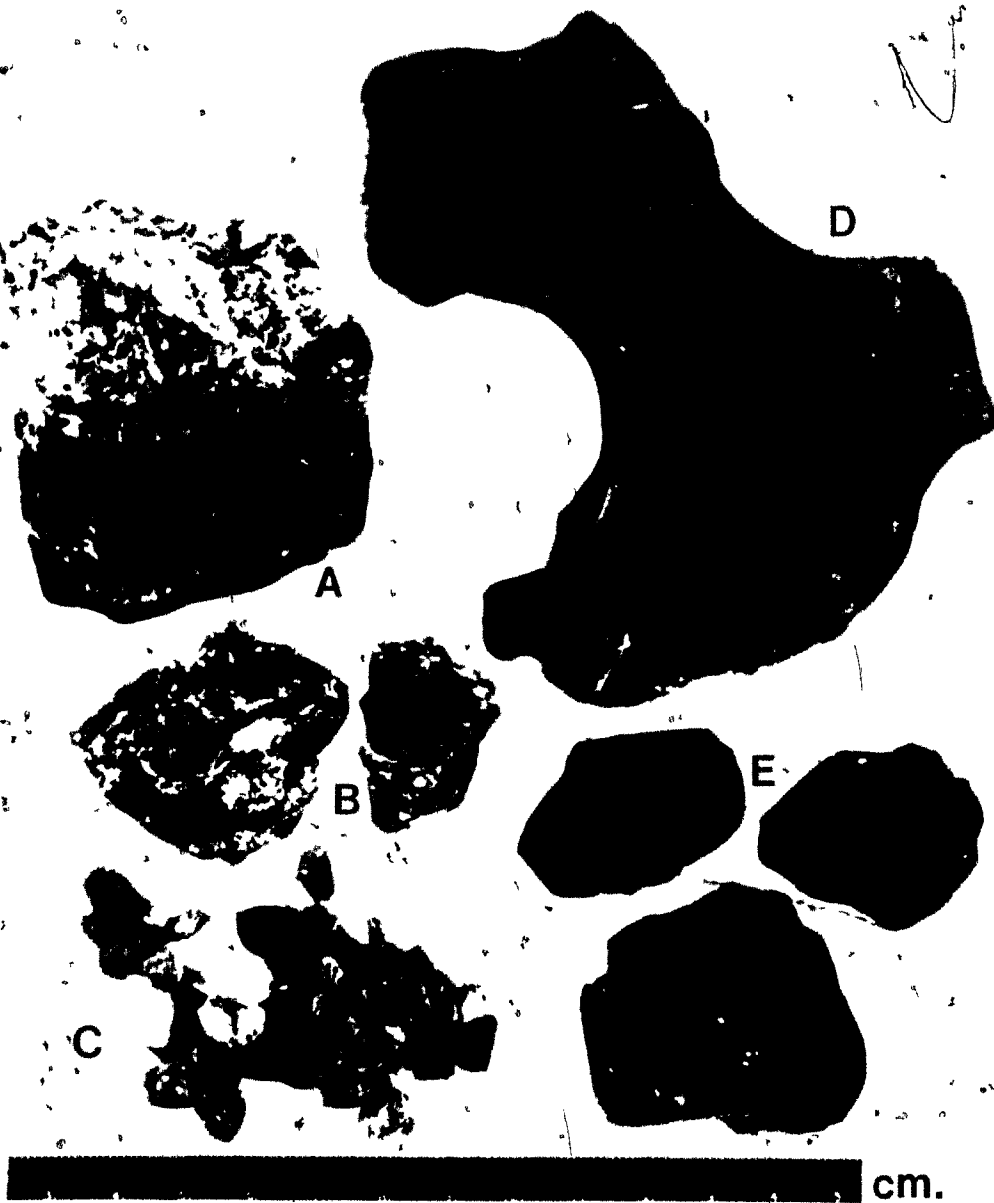


Table A1

Bulk Composition of the Apatites (wt. %)

	Mexican	Ontario	Quebec	Florida	Marine (PD1930)
P ₂ O ₅	35.47	34.98	29.58	28.17	22.66
CaO	46.96	53.72	48.84	41.99	34.64
CO ₂	1.16	1.70	7.29	5.08	3.18
Fe ₂ O ₃	0.32	0.44	0.56	1.31	3.16
Al ₂ O ₃	1.29	0.11	0.83	1.10	4.47
MgO	0.14	0.10	2.52	0.50	1.15
Na ₂ O	0.25	0.12	0.14	0.69	1.99
K ₂ O	0.33	0.02	0.35	0.23	0.76
F	2.93	6.28	2.19	2.97	2.68
total	88.6	97.5	92.3	83.0	74.69
-O=F	1.23	2.64	0.92	1.67	1.13
total	88.4	94.9	91.4	81.3	75.6

Using the method outlined in Deer et al. (1966), the bulk chemical formulae were calculated to be:

Mexican	Ca _{8.5} Na _{0.08} K _{0.07} (PO ₄) _{5.1} (CO ₃) _{0.27} F _{1.6}
*Ontario	Ca _{8.4} (PO ₄) _{4.3} (CO ₃) _{0.34} F _{2.9} (OH) _{0.7}
*Quebec	Ca _{8.9} K _{0.8} Mg _{0.64} (PO ₄) _{4.3} (CO ₃) _{1.7} F _{1.2} (OH) _{4.07}
Florida	Ca _{7.7} Na _{0.23} Mg _{0.13} K _{0.05} (PO ₄) _{4.1} (CO ₃) _{1.5} F _{2.2}
*Marine	Ca _{7.8} Na _{0.8} Mg _{0.4} K _{0.2} (PO ₄) _{4.0} (CO ₃) _{0.4} F _{1.8} (OH) _{3.2}

* Hydroxyls added to balance charge.

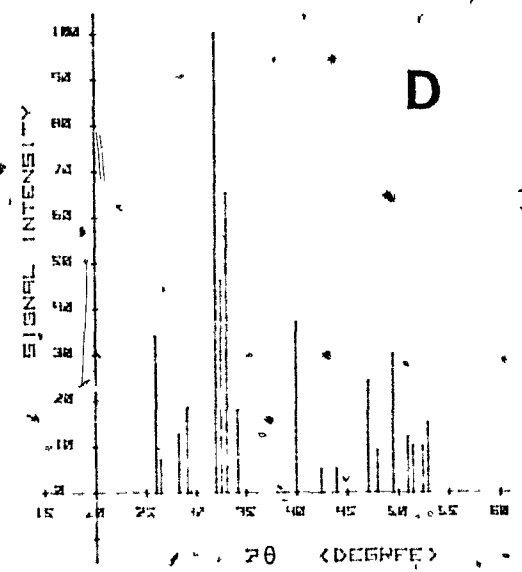
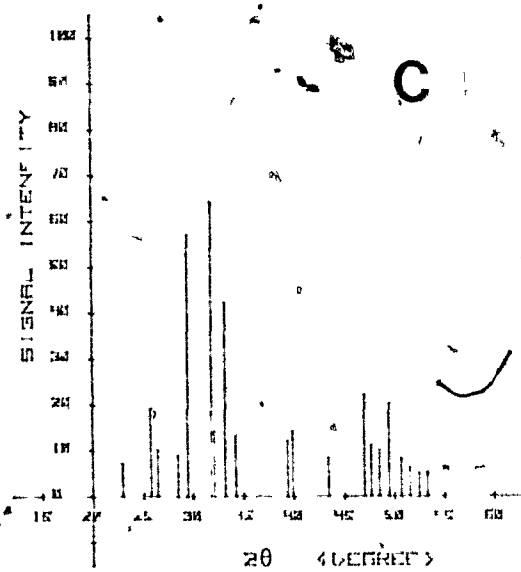
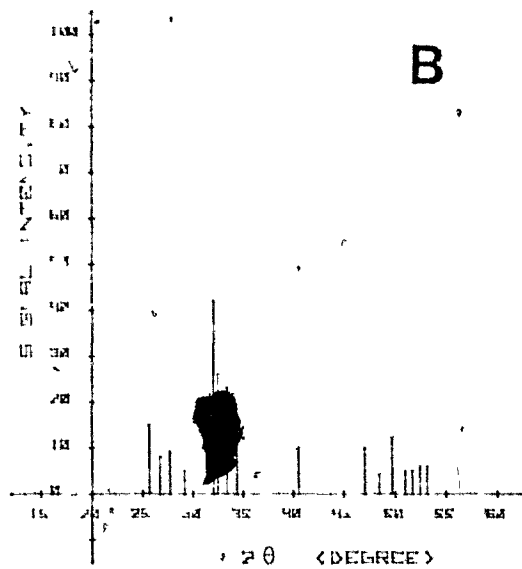
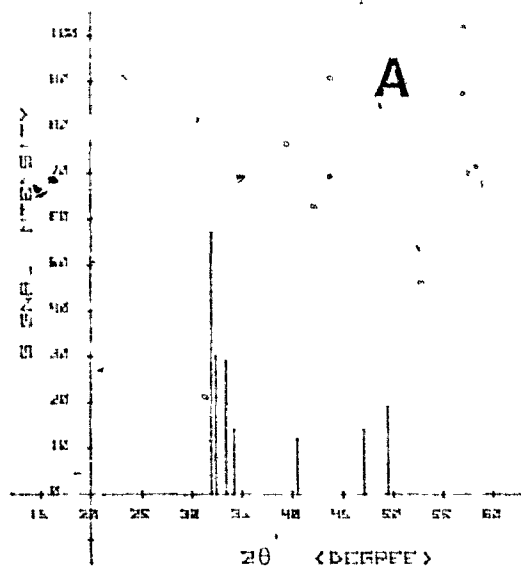
Figure A2

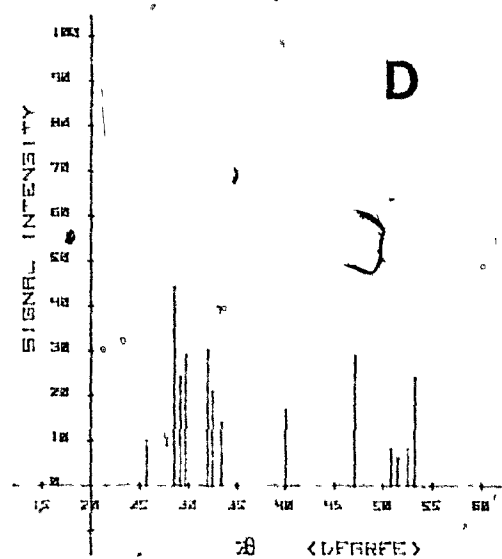
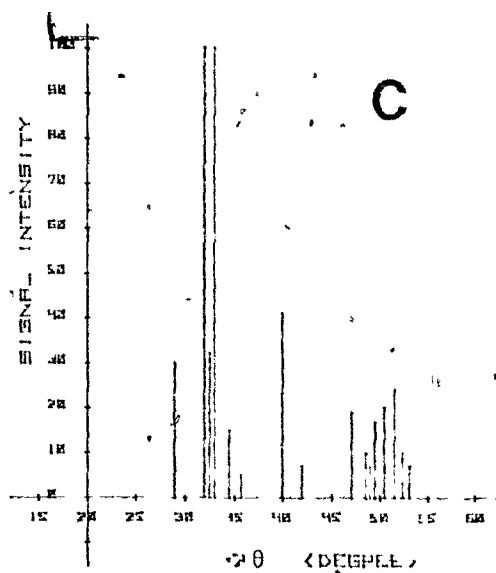
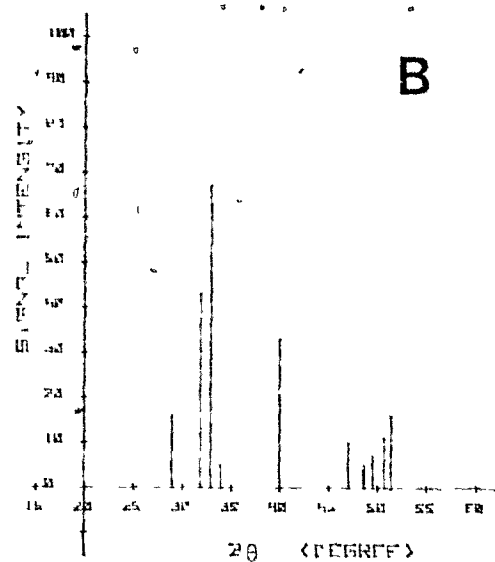
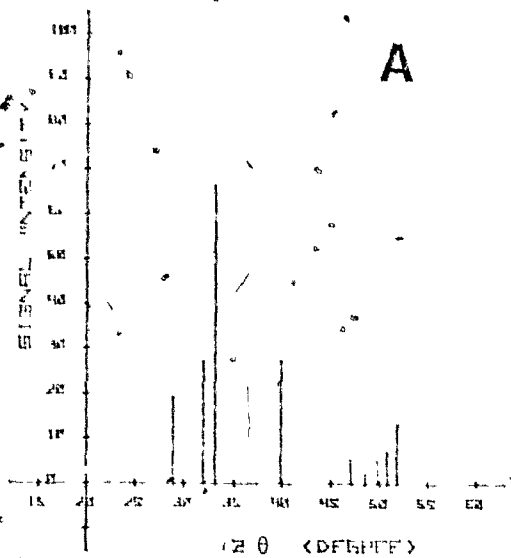
X-ray Powder Diffraction Patterns*

- I. A. Hydroxyapatite Exposed** to Seawater + 500 ppm NaF
- B. Hydroxyapatite
- C. Hydroxyapatite Exposed to Seawater
- II. A. Mexico Apatite
- B. Mexico Apatite Exposed to Seawater
- C. Ontario Apatite
- D. Ontario Apatite Exposed to Seawater
- III. A. Marine Phosphorite
- B. Marine Phosphorite Exposed to Seawater + 500 ppm NaF
- C. Quebec Apatite
- D. Florida Pebble Collophane

* (Samples were finely ground, made into a slurry in acetone and deposited on glass slides)

** (Exposure times in seawater were 192 hours at 1 atm., 2°C)





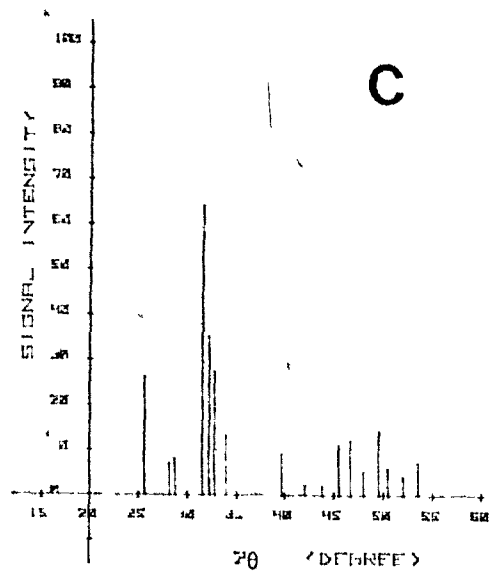
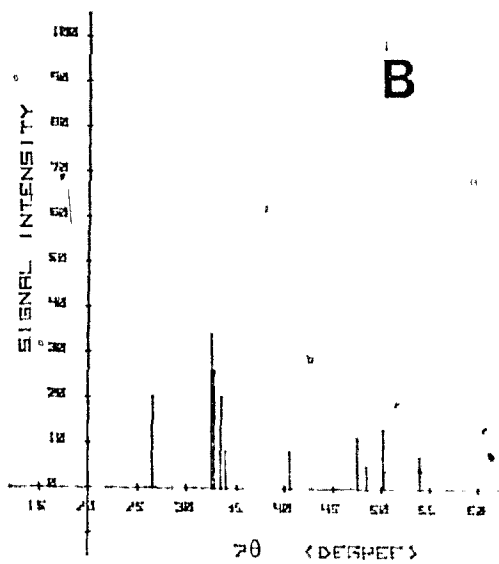
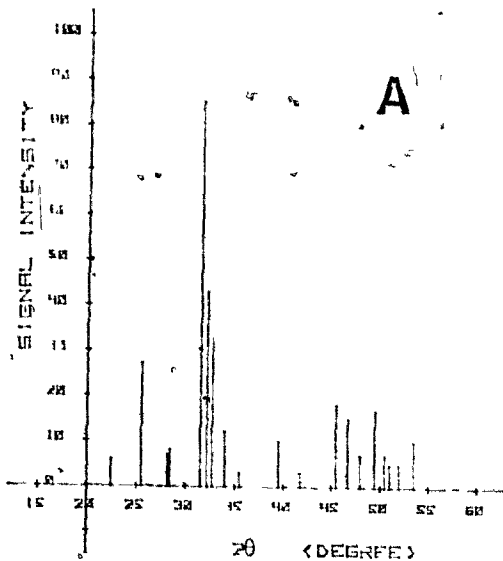


Figure A3

I. a, b Mexican Apatite Unreacted

c, d Quebec Apatite Unreacted

e, f Florida Pebble Collphane Unreacted

II. Marine Apatite Unreacted

III. Examples of Test Remains in the Marine Apatite

a - c Diatom Test

d - f Choanoflagellate Test

IV. Ontario Apatite Unreacted



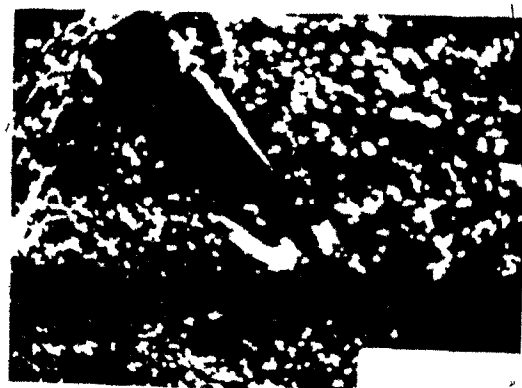
a



b



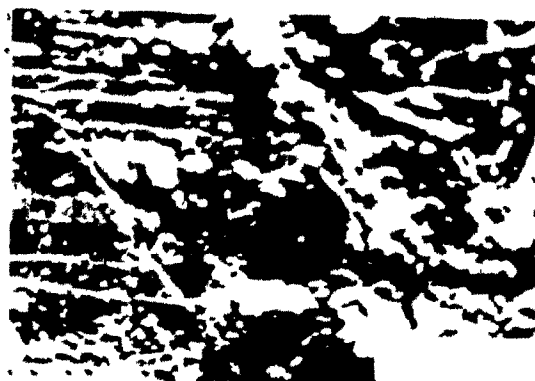
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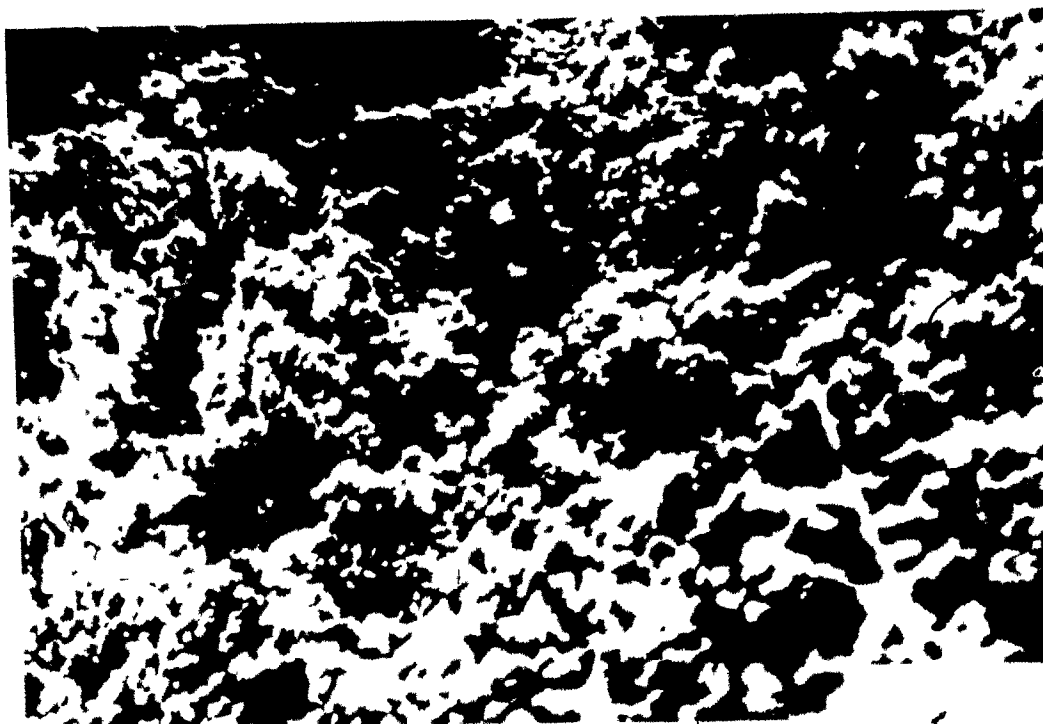
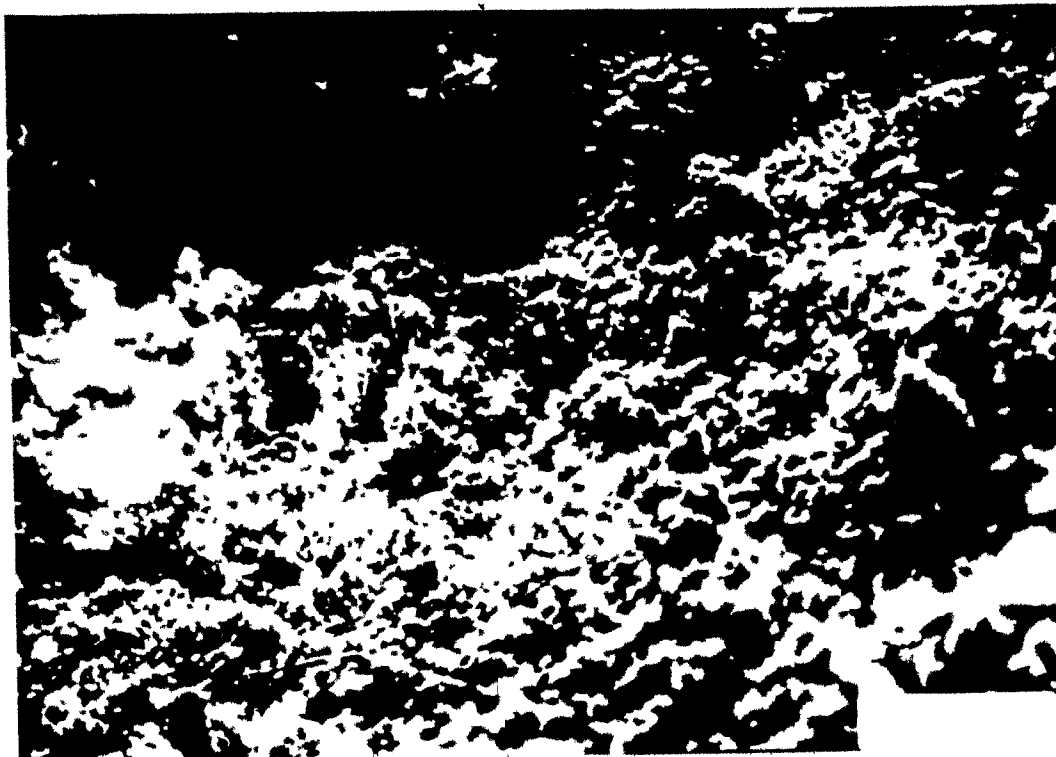


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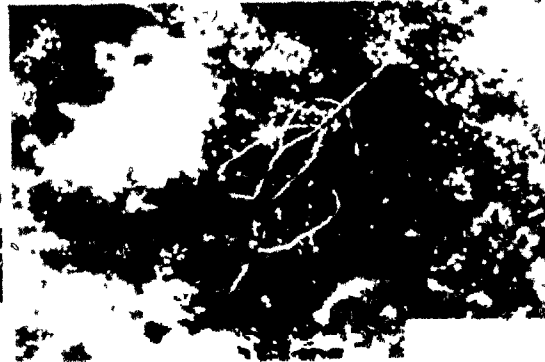
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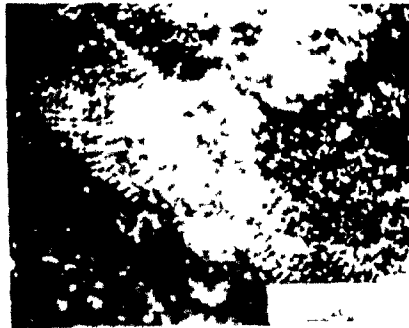




a



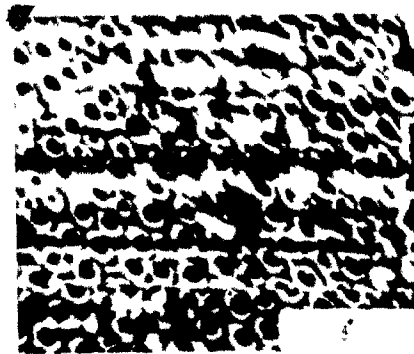
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b



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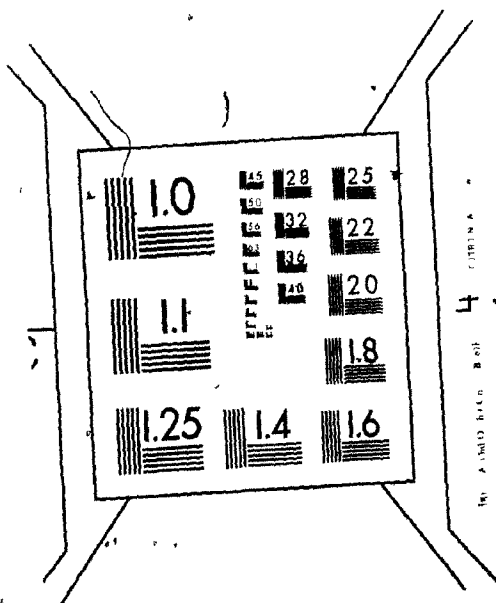


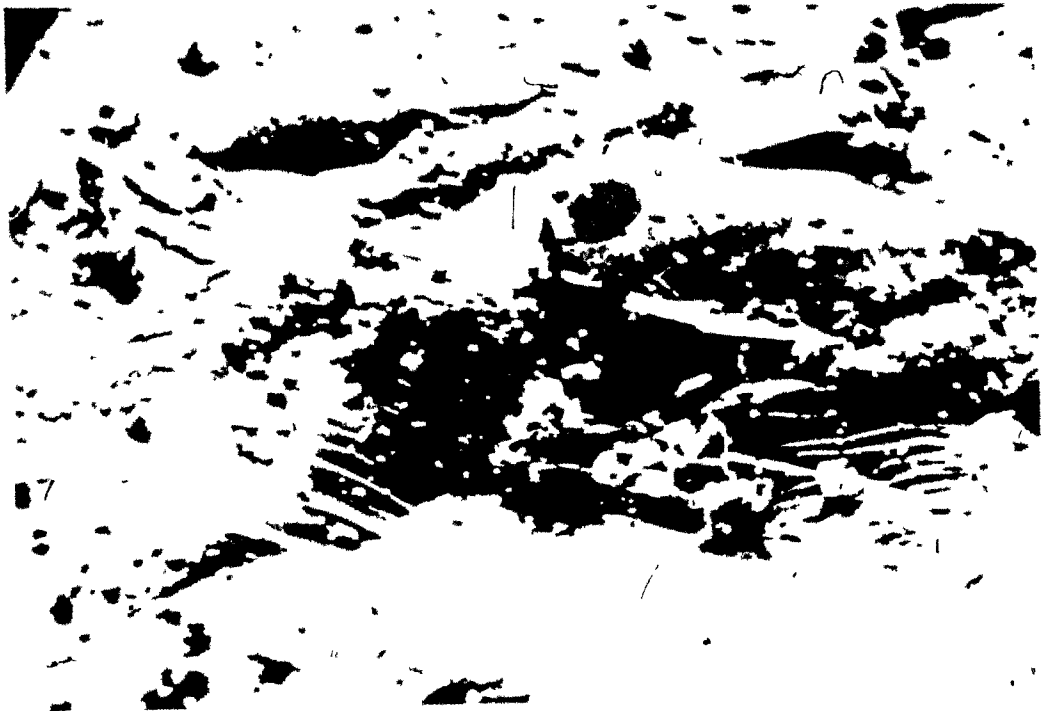
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APPENDIX B: Dissolution Data

TABLE B1 (a)

Experiment Temperature Variation

Solution 0.65 N NaCl (1 atm, initial pH set to 8.2)

Apatite Mexico (8-28 mesh, 10g/100cc)

Temperature (°C)	Conc (M)	Time (Hours)						
		0	2	6	48	72	120	192
2	$\text{TPO}_4 \times 10^{-4}$	0.03	2.4	5.8	13.4	12.9	17.7	21.8
	$\text{F} \times 10^{-5}$	0.0	0.7	2.6	7.4	-	13.8	16.5
	$\text{OH} \times 10^{-7}$	7.3	0.68	0.78	3.1	9.3	2.5	7.1
	$\text{Ca} \times 10^{-4}$	0.0	0.83	1.68	25.7	25.0	23.1	44.7
25	$\text{TPO}_4 \times 10^{-5}$	0.03	2.2	5.4	6.76	6.51	6.3	7.63
	$\text{F} \times 10^{-5}$	0	0.7	2.1	4.3	6.9	5.4	5.2
	$\text{OH} \times 10^{-7}$	16.0	0.18	0.98	1.7	0.4	0.71	1.0
	$\text{Ca} \times 10^{-4}$	0	0.97	1.07	1.67	2.06	1.6	2.4

Apatite Ontario (as above)

2	$\text{TPO}_4 \times 10^{-5}$	0.03	0.67	1.8	14.2	15.6	16	23.9
	$\text{F} \times 10^{-5}$	0	1.1	1.1	6.9	5.5	9.4	16.2
	$\text{OH} \times 10^{-6}$	7.3	0.24	1.0	4.6	2.7	2.3	-
	$\text{Ca} \times 10^{-4}$	0	0.75	3.0	5.4	5.5	5.5	6.8
25	$\text{TPO}_4 \times 10^{-6}$	0.03	1.8	6.1	4.5	7.1	7.5	4.7
	$\text{F} \times 10^{-5}$	0	0.9	0.6	0.96	1.2	1.1	1.05
	$\text{OH} \times 10^{-7}$	16	0.32	1.8	1.5	1.3	1.7	2.4
	$\text{Ca} \times 10^{-4}$	0	1.1	1.2	1.7	4.9	3.0	3.1

Apatite. Quebec (as above)

2	$\text{TPO}_4 \times 10^{-5}$	0.03	0.27	0.47	2.4	1.7	3.5	4.3
	$\text{F} \times 10^{-5}$	0	0.35	0.70	2.6	1.7	-	3.7
	$\text{OH} \times 10^{-6}$	7.3	1.79	2.1	4.6	5.1	6.5	2.3
	$\text{Ca} \times 10^{-4}$	0	9.1	14.5	16.45	14.6	-	12.4
25	$\text{TPO}_4 \times 10^{-6}$	0.03	1.1	1.0	5.1	3.9	3.9	-
	$\text{F} \times 10^{-6}$	0	6.3	4.6	12.5	8.6	8.7	-
	$\text{OH} \times 10^{-6}$	16.0	1.6	5.4	7.5	-	1.8	4.5
	$\text{Ca} \times 10^{-4}$	0	14.8	-	-	-	14.2	13.0

TABLE B1 (b)

Experiment Temperature Variation

Solution Seawater (1 atm)

Apatite Mexico (8-28 mesh, 10g/100cc)

Temperature (°C)	Conc (M)	Time (Hours)						
		0	2	6	48	72	120	192
2	$\text{TPO}_4 \times 10^{-5}$	0.4	0.88	0.88	4.5	3.7	4.0	10.1
	$\text{F} \times 10^{-5}$	2.75	4.4	4.1	4.7	4.6	5.35	3.9
	$\text{OH} \times 10^{-7}$	-	2.8	2.5	4.3	3.4	5.2	2.2
	$\text{Ca} \times 10^{-3}$	10.7	8.1	8.8	8.2	8.3	8.2	6.8
25	$\text{TPO}_4 \times 10^{-5}$	0.3	1.0	2.0	5.0	9.4	10.0	9.5
	$\text{F} \times 10^{-5}$	2.75	2.75	2.75	3.75	5.7	5.7	3.5
	$\text{OH} \times 10^{-7}$	6.1	-	4.7	6.2	6.4	7.6	6.1
	$\text{Ca} \times 10^{-3}$	11.3	8.3	7.6	8.4	8.5	7.8	8.1

Apatite Ontario (as above)

2	$\text{TPO}_4 \times 10^{-5}$	0.2	0.4	1.6	0.7	4.9	15.0	10.5
	$\text{F} \times 10^{-5}$	2.3	3.4	3.4	4.1	5.0	10.0	8.9
	$\text{OH} \times 10^{-7}$	-	2.6	4.4	2.9	3.3	6.5	4.5
	$\text{Ca} \times 10^{-3}$	9.2	9.2	9.2	9.6	8.6	-	8.6
25	$\text{TPO}_4 \times 10^{-6}$	2.0	3.0	1.4	2.3	4.7	5.5	4.5
	$\text{F} \times 10^{-5}$	2.3	3.4	4.1	4.6	4.6	4.8	4.6
	$\text{OH} \times 10^{-7}$	-	1.3	7.3	5.7	4.8	4.7	8.0
	$\text{Ca} \times 10^{-3}$	9.2	10.9	10.5	9.8	7.2	8.8	10.6

Apatite Quebec (as above)

2	$\text{TPO}_4 \times 10^{-5}$	0.2	0.2	0.3	0.4	1.7	4.7	3.2
	$\text{F} \times 10^{-5}$	2.3	3.2	3.8	4.5	4.2	3.4	5.7
	$\text{OH} \times 10^{-7}$	-	3.5	3.6	2.8	3.9	15.3	10.6
	$\text{Ca} \times 10^{-3}$	9.2	-	12.7	13.5	13.9	-	9.3
25	$\text{TPO}_4 \times 10^{-6}$	2.	2.1	1.2	6.0	3.7	3.9	6.1
	$\text{F} \times 10^{-5}$	2.3	2.8	4.0	-	4.6	3.6	5.0
	$\text{OH} \times 10^{-7}$	-	4.2	8.0	9.2	7.6	4.9	14.7
	$\text{Ca} \times 10^{-3}$	9.2	13.8	11.6	10.7	8.2	11.5	10.2

Apatite Floride

(as above)

2	$\text{TPO}_4 \times 10^{-5}$	0.2	1.5	5.8	3.0	4.4	3.0	2.3
	$\text{F} \times 10^{-5}$	2.3	4.6	4.1	5.8	6.1	5.1	6.3
	$\text{OH} \times 10^{-7}$	14.	2.8	3.0	1.9	2.1	-	3.7
	$\text{Ca} \times 10^{-3}$	8.9	8.3	7.6	8.5	8.4	8.3	8.0
25	$\text{TPO}_4 \times 10^{-5}$	0.12	0.19	0.15	2.0	3.4	5.1	9.1
	$\text{F} \times 10^{-5}$	4.5	4.7	5.0	5.4	6.0	6.0	6.8
	$\text{OH} \times 10^{-8}$	22	8.7	14.9	10.8	9.2	4.6	7.0
	$\text{Ca} \times 10^{-3}$	9.3	8.3	7.9	8.4	8.5	6.8	7.1

TABLE B2 (a)

Experiment: Pressure Variations

Solution 0.65 N NaCl or Seawater (5-6°C)

Apatite Mexico (8-28 mesh, column 18 cm x 1-cm ID)

Solution	Conc (M)	Pressure (atm.)															
		Up								Down							
		INIT	30	90	190	340	500	660	820	1000	820	660	500	340	190	90	30
0.65 N NaCl	$\text{TPO}_4 \times 10^{-6}$	0.25	-	-	11.7	16.1	22.7	34.0	41.8	50.7	42.5	32.4	25.9	23.1	17.8	14.8	12.2
	$\text{F} \times 10^{-6}$	1.0	-	14.7	15.1	17.0	17.0	21.7	22.2	25.7	27.2	23.2	22.4	20.7	16.6	15.4	14.0
	$\text{OH} \times 10^{-7}$	-	0.19	1.3	3.0	-	9.6	10.0	14.2	-	16.6	-	10.3	10.5	12.3	-	10.5
	$\text{Ca} \times 10^{-5}$	0.63	-	-	-	12.7	13.0	14.4	15.3	18.6	16.6	14.7	15.2	14.3	13.6	12.5	12.1
Sea- water	$\text{TPO}_4 \times 10^{-6}$	1.8	3.15	3.27	-	4.25	4.70	-	6.76	7.70	6.74	6.15	5.10	3.08	2.18	1.92	1.94
	$\text{F} \times 10^{-5}$	2.3	4.40	4.04	4.58	4.63	4.60	6.10	6.17	6.46	5.23	4.90	4.74	4.03	3.9	3.45	2.9
	$\text{OH} \times 10^{-8}$	-	10.7	12.0	10.0	11.8	12.3	13.8	12.7	15.0	15.3	12.3	12.2	14.6	12.9	11.7	6.5
	$\text{Ca} \times 10^{-3}$	9.1	-	9.11	-	9.04	10.81	10.0	-	12.7	11.34	10.56	9.83	11.11	11.38	11.63	11.18

Apatite: Ontario (as above)

0.65 N NaCl	$\text{TPO}_4 \times 10^{-6}$	0.25	-	-	2.55	2.81	3.04	3.43	3.60	4.42	3.15	2.95	2.50	2.24	-	1.45	1.40
	$\text{F} \times 10^{-6}$	1.5	-	10.5	10.1	-	14.3	19.6	19.2	19.2	17.1	18.3	16.6	18.7	16.3	15.6	15.2
	$\text{OH} \times 10^{-6}$	-	-	7.4	8.5	-	8.3	11.0	11.5	15.8	14.5	13.6	12.0	9.1	.85	5.6	5.1
	$\text{Ca} \times 10^{-4}$	0.03	-	-	5.35	4.8	5.79	6.06	7.35	9.44	8.49	7.89	6.61	6.47	5.12	4.64	4.35
Sea- water	$\text{TPO}_4 \times 10^{-6}$	1.8	1.58	1.54	-	1.91	2.21	-	3.21	3.51	2.82	2.66	2.22	1.77	1.38	1.28	1.24
	$\text{F} \times 10^{-5}$	2.3	3.30	3.04	3.59	3.60	3.89	-	4.32	4.10	3.94	-	3.85	3.40	3.50	3.30	3.09
	$\text{OH} \times 10^{-8}$	-	6.31	8.5	6.8	8.7	10.	14.3	13.3	14.0	15.49	4.8	8.7	7.08	-	6.9	3.55
	$\text{Ca} \times 10^{-3}$	9.1	-	11.26	10.14	10.12	10.41	-	11.39	11.88	11.17	9.77	9.50	10.15	10.93	11.13	11.51

TABLE B2 (a) Continued

Experiment: Pressure Variations

Solution: 0.65 N NaCl or Seawater or Seawater 500 ppm NaF (5-6°C)

Apatite: Marine Phosphorite

Solution	Conc. (M)	Pressure (atm.)															
		Up								Down							
		INIT	30	90	190	340	500	640	820	1000	820	660	500	340	190	90	30
0.65 N NaCl	$\text{TPO}_4 \times 10^{-5}$	0.07	6.98	-	7.0	10.15	10.15	10.15	15.1	14.9	11.1	9.05	8.2	8.5	6.9	4.3	4.86
	$\text{F} \times 10^{-5}$	0.14	3.93	2.45	2.63	4.17	5.27	6.67	7.78	12.3	9.55	12.5	9.55	10.05	8.94	6.53	10.6
	$\text{OH} \times 10^{-9}$	46	-	5.38	5.38	-	-	5.6	4.38	5.26	4.8	4.13	4.18	4.0	3.48	3.32	2.89
	$\text{Ca} \times 10^{-3}$	0	7.93	-	8.59	-	6.19	7.33	7.61	7.44	4.44	5.48	4.38	4.16	3.56	3.12	-
Sea-water	$\text{TPO}_4 \times 10^{-5}$	0.38	3.9	-	-	4.28	-	3.9	2.95	4.69	-	-	5.88	3.35	-	4.35	3.53
	$\text{F} \times 10^{-5}$	3.55	2.69	3.77	2.24	2.52	4.8	-	5.08	5.5	-	-	5.4	-	-	-	3.3
	$\text{OH} \times 10^{-9}$	8.1	-	3.4	-	-	1.05	1.74	2.7	2.5	2.3	-	1.70	1.55	1.20	1.10	-
	$\text{Ca} \times 10^{-3}$	9.0	-	13.1	15.7	14.6	20.7	-	27.6	19.9	14.3	-	15.7	14.8	11.3	11.9	-
Sea-water + 500 ppm NaF	$\text{TPO}_4 \times 10^{-5}$	-	-	3.6	-	-	-	-	-	2.31	5.4	-	5.52	2.5	5.0	2.6	-
	$\text{F} \times 10^{-4}$	51.5	-	0.73	-	1.31	-	-	-	-	1.78	-	1.46	1.70	1.49	0.65	-
	$\text{OH} \times 10^{-9}$	-	-	1.9	-	1.05	-	1.45	1.55	1.52	1.52	-	1.29	1.29	0.89	0.81	-
	$\text{Ca} \times 10^{-3}$	-	-	15.7	-	23.7	-	31.9	22.5	15.7	15.7	-	15.3	14.1	12.2	11.3	-

TABLE B2 (b)

Experiment: Pressure and Temperature Variations

Solution 0.65 N NaCl

Agarite: Mexico (8-28 mesh, column 18 cm x 1 cm ID)

Temperature (°C)	Conductivity (m)	Pressure (atm.)													
		Up							Down						
		INIT	30	90	190	340	500	660	820	1000	820	660	500	340	30
5-6	$\text{TPO} \times 10^{-6}$	0.25	-	-	11.7	16.1	22.7	34.0	41.8	50.7	42.5	32.4	25.9	23.1	17.8
	$\text{F} \times 10^{-6}$	1.0	-	14.7	15.1	17.0	17.0	21.7	22.2	25.7	27.2	23.2	22.4	20.7	16.6
	$\text{OH} \times 10^{-7}$	-	0.19	1.3	3.0	-	9.6	10.0	14.2	6.3	16.6	6.3	10.3	10.5	12.3
	$\text{Ca} \times 10^{-5}$	0.63	-	-	-	12.7	13.0	14.4	15.3	18.6	16.6	14.7	15.2	14.3	13.6
14	$\text{TPO} \times 10^{-6}$	0.25	6.8	6.05	6.1	10.5	14.0	19.6	21.2	-	-	15.8	-	-	-

TABLE B3

Experiment: NaCl Solution + Spikes for Common Ion Effects

Solution: 0.65 N NaCl + Spikes (1 atm., 2°C)

Apatite: Ontario (8-28 mesh, 5g/100cc)

Spike (M)	Conc. (M)	Time (Hours)							
		0	3	6	10	24	72	115	192
1×10^{-4} (CaCO ₃)	TPO ₄ x 10 ⁻⁵	0.1	0.7	1.7	0.47	1.4	0.32	0.8	7.4
	F x 10 ⁻⁵	1.9	2.3	1.45	-	3.1	2.1	8.9	8.5
	OH x 10 ⁻⁷	1.2	3.1	2.1	7.8	270.	110.	330.	110.
	Ca x 10 ⁻⁴	1.5	2.1	2.8	3.9	2.2	3.7	3.8	4.5
1×10^{-2} (CaCO ₃)	TPO ₄ x 10 ⁻⁵	0.5				2.6	1.1	2.3	-
	F x 10 ⁻⁵	0.9				2.4	-	4.4	5.8
	OH x 10 ⁻⁶	3.6				5.3	13.	42.	28.
	Ca x 10 ⁻³	10.1				15.3	15.9	13.	9.3
2.4×10^{-3} (NaF)	TPO ₄ x 10 ⁻⁶	6.3	7.	11.2	14.	10.6	16.9	-	93.2
	F x 10 ⁻³	11.5	12.1	15.1	15.2	11.0	-	14.6	10.2
	OH x 10 ⁻⁶	0.3	2.0	2.5	14.	24.	40.	39.	27
	Ca x 10 ⁻⁵	1.5	17.7	11.4	15.3	33.4	22.8	-	29.6
5×10^{-5} (K ₂ HPO ₄)	TPO ₄ x 10 ⁻⁵	3.4	3.3	4.7	6.3	4.9	6.0	7.0	9.3
	F x 10 ⁻⁵	1.0	5.9	2.6	3.1	-	11.5	-	10.2
	OH x 10 ⁻⁶	0.002	0.006	0.8	8.1	1.6	27.	25.	27.
	Ca x 10 ⁻⁵	1.8	15.6	12.4	16.2	26.3	25	25.6	29.6

TABLE B4

Experiment Variation of Solid Amount/100. cc Solution

Solution: Seawater (1 atm., 2°C)

Apatite Mexico (8-28 mesh)

Amt of Solid (g)	Conc. (M)	Time (Hours)						
		0	4	7	24	72	120	192
0.1	$\text{TPO}_4 \times 10^{-6}$	1.55	1.47	1.95	1.46	-	1.28	1.6
	$\text{F} \times 10^{-5}$	3.6	4.7	6.6	5.9	3.7	4.5	5.3
	$\text{OH} \times 10^{-7}$	2.6	2.7	3.3	3.1	4.6	3.7	4.7
	$\text{Ca} \times 10^{-3}$	8.4	8.6	8.4	8.2	7.5	7.8	7.8
0.5	$\text{TPO}_4 \times 10^{-6}$	1.55	0.8	0.8	1.5	1.0	1.5	3.3
	$\text{F} \times 10^{-5}$	3.6	6.2	4.3	9.1	5.2	4.7	4.0
	$\text{OH} \times 10^{-7}$	2.6	3.	2.7	2.7	4.9	3.7	4.5
	$\text{Ca} \times 10^{-3}$	8.4	8.7	9.5	8.0	8.3	8.6	9.1
1.0	$\text{TPO}_4 \times 10^{-6}$	1.55	0.4	1.7	2.3	1.6	4.9	7.8
	$\text{F} \times 10^{-5}$	3.6	4.6	5.9	7.7	4.7	3.6	4.0
	$\text{OH} \times 10^{-7}$	2.6	3.3	3.3	3.1	4.9	3.5	4.0
	$\text{Ca} \times 10^{-3}$	8.4	8.0	8.1	7.6	7.5	6.9	7.9
5.0	$\text{TPO}_4 \times 10^{-6}$	1.6	6.7	6.6	7.5	19.9	17.9	37.
	$\text{F} \times 10^{-5}$	3.6	6.1	4.5	3.8	4.0	4.3	5.0
	$\text{OH} \times 10^{-7}$	2.6	2.9	2.7	2.5	4.3	2.8	3.2
	$\text{Ca} \times 10^{-3}$	8.4	9.4	8.7	7.2	8.0	7.8	8.4
10.0	$\text{TPO}_4 \times 10^{-5}$	0.16	0.88	0.85	4.3	3.7	4.0	10.5
	$\text{F} \times 10^{-5}$	2.75	4.35	4.1	4.7	4.6	5.2	3.9
	$\text{OH} \times 10^{-7}$	-	2.75	2.45	4.3	3.4	5.2	2.2
	$\text{Ca} \times 10^{-3}$	10.7	8.05	8.8	8.15	8.3	8.2	6.8

TABLE B5

Experiment: To Test Effects of Crushing During Sample Preparation

Solution: Seawater (1 atm., 2°C)

Apatite: Marine (10g/100cc)

Solid Description	Conc. (M)	Time (Hours)								
		0	2	6	24	48	72	120	192	240
Un-ground	$\text{TPO}_4 \times 10^{-6}$		4.9			9.9	6.2	8.6	9.2	16.4
	$\text{F} \times 10^{-5}$		5.03			4.3	4.2	5.5	5.3	5.6
	$\text{OH} \times 10^{-7}$		4.4			0.74	3.1	1.6	0.7	1.5
	$\text{Ca} \times 10^{-3}$		10.2			10.3	9.3	8.8	8.4	9.6
Ground * to 8-28 Mesh	$\text{TPO}_4 \times 10^{-5}$	0.16	0.6	0.7		2.3		2.9	-	4.6
	$\text{F} \times 10^{-5}$	3.6	9.0	8.6		7.3		5.9	4.9	7.7
	$\text{OH} \times 10^{-8}$	26.	9.2	4.6		4.9		3.8	2.6	6.2
	$\text{Ca} \times 10^{-3}$	8.4	8.7	9.0		10.7		10.9	10.3	-
Ground* to 48-60 Mesh	$\text{TPO}_4 \times 10^{-5}$	0.15	1.74		2.2		2.75	-	2.14	
	$\text{F} \times 10^{-5}$	7.4	8.9		11.5		10.2	6.5	6.1	
	$\text{OH} \times 10^{-8}$	55.4	22.		4.0		1.2	1.6	1.3	
	$\text{Ca} \times 10^{-3}$	12.3	13.9		21		16.	22.5	19.	

* Ground refers to material ground in a machine using ceramic grinding wheels and sieved to appropriate mesh.

TABLE B6

Experiment Variation of TPO_4 in Solution
 Solution: Seawater + K_2HPO_4 (1 atm., 2°C)

Apatite: Mexico (8-28 mesh, 50g/1000cc)

TPO ₄ Spike (M)	Conc. (M)	Time (Hours)						
		0	1	5	10	24	48	192
25 x 10 ⁻⁶	TPO ₄ x 10 ⁻⁴		0.38	0.03	1.5	3.5	6.9	6.2
	F x 10 ⁻⁵		4.1	4.2	7.0	11.5	18.4	40.3
	OH x 10 ⁻⁷		1.0	1.5	1.0	2.3	7.0	12.0
	Ca x 10 ⁻³		11.4	7.9	8.3	9.8	8.5	9.5
50 x 10 ⁻⁶	TPO ₄ x 10 ⁻⁴	0.21	0.47	0.89	1.6	3.8	7.7	6.3
	F x 10 ⁻⁵	2.0	3.9	3.8	6.7	12.6	19.5	53.1
	OH x 10 ⁻⁷	14.2	5.8	1.5	1.4	3.1	3.7	7.3
	Ca x 10 ⁻³	9.1	11.6	7.1	8.3	8.3	7.9	10.9

Apatite: Quebec (as above)

25×10^{-6}	$\text{TPO}_4 \times 10^{-4}$		0.19	0.41	0.89	1.9	3.1	2.7
	F $\times 10^{-5}$		3.6	3.0	5.0	7.4	7.5	-
	OH $\times 10^{-7}$		5.5	1.8	0.84	7.0	8.6	18.
	Ca $\times 10^{-3}$		11.9	8.6	9.3	10.3	8.6	12.3
50×10^{-6}	$\text{TPO}_4 \times 10^{-4}$	0.21	0.56	0.51	0.52	0.39	0.45	1.59
	F $\times 10^{-5}$	2.0	5.6	4.5	4.6	4.2	4.2	4.6
	OH $\times 10^{-7}$	14.2	8.4	6.1	6.2	4.8	8.8	6.2
	Ca $\times 10^{-3}$	9.1	7.8	7.9	8.3	8.4	8.1	8.4

Apatite: Florida (as above)

25×10^{-6}	$\text{TPO}_4 \times 10^{-5}$		4.9	5.3	-	3.2	3.0	2.6
	F $\times 10^{-5}$		5.2	4.1	6.8	-	6.9	6.2
	OH $\times 10^{-7}$		1.8	2.9	2.0	1.7	4.8	3.6
	Ca $\times 10^{-3}$		7.8	7.2	7.1	7.8	7.0	7.4
50×10^{-6}	$\text{TPO}_4 \times 10^{-5}$		4.4	-	8.9	4.2	3.3	5.2
	F $\times 10^{-5}$		4.5	3.8	6.2	4.9	5.7	6.1
	OH $\times 10^{-7}$		2.6	2.3	2.0	2.0	3.1	3.3
	Ca $\times 10^{-3}$		8.2	8.1	8.0	7.9	6.8	8.4

TABLE B7

Experiment. Low-level Variation of Fluoride in Solution

Solution: Seawater + NaF (1 atm., 2°C)

Apatite. Florida (8-28 mesh, 5g/100cc)

NaF Spike (ppm)	Conc. (M)	Time (Hours)						
		0	1	5	10	24	48	192
0.35	$\text{TPO}_4 \times 10^{-5}$	0.12	0.79	-	0.47	0.52	1.45	2.3
	$\text{F} \times 10^{-5}$	2.9	4.7	4.9	5.3	4.6	5.1	6.1
	$\text{OH} \times 10^{-7}$	-	5.5	5.1	4.4	2.6	2.7	1.8
	$\text{Ca} \times 10^{-3}$	-	8.0	7.2	7.0	8.0	8.4	8.4
3.5	$\text{TPO}_4 \times 10^{-5}$	0.12	16.4	1.9	5.7	-	6.0	3.0
	$\text{F} \times 10^{-5}$	10.4	9.4	8.5	9.0	8.4	8.3	9.1
	$\text{OH} \times 10^{-7}$	-	5.7	2.8	4.6	3.7	3.7	1.9
	$\text{Ca} \times 10^{-3}$	-	8.3	8.1	8.2	8.2	8.7	8.0

TABLE B8 (a)

Experiment. High-Level Variation in Fluoride, Low Temperature

Solution. Seawater + NaF (1 atm., 2°C)

Apatite. Mexico (8-28 mesh, 5g/100cc)

NaF Spike (ppm)	Conc. (M)	Time (Hours)								
		0	2	6	10	24	96	192		
100	$\text{TPO}_4 \times 10^{-6}$		0.25	0.25	0.88	0.63	23.8	22.5		
	$\text{F} \times 10^{-3}$		1.6	1.5	1.5	1.8	1.5	1.5		
	$\text{OH} \times 10^{-7}$		5.3	3.7	3.3	3.0	3.3	3.6		
	$\text{Ca} \times 10^{-3}$		7.7	7.5	8.0	7.9	8.0	7.8		
500	$\text{TPO}_4 \times 10^{-6}$		1.25	-	-	-	-	1.9		
	$\text{F} \times 10^{-3}$		6.3	4.9	4.9	-	2.8	3.0		
	$\text{OH} \times 10^{-7}$		2.5	2.4	2.0	4.0	2.0	1.7		
	$\text{Ca} \times 10^{-3}$		6.9	6.0	6.3	6.1	5.3	5.3		
Apatite: Ontario (as above)		0	2	6	10	24	72	153	192	
100	$\text{TPO}_4 \times 10^{-6}$		1.2	-	-	-	2.6	16	23.1	
	$\text{F} \times 10^{-3}$		1.45	1.6	1.6	1.9	1.7	1.7	1.8	
	$\text{OH} \times 10^{-7}$		4.6	4.8	-	3.8	4.3	4.7	4.6	
	$\text{Ca} \times 10^{-3}$		7.45	7.6	7.3	7.5	8.0	7.9	7.9	
500	$\text{TPO}_4 \times 10^{-6}$		0.25	0.25	0.25	0.25	-	2.9	3.0	
	$\text{F} \times 10^{-3}$		6.4	6.0	5.8	6.6	4.2	3.2	2.7	
	$\text{OH} \times 10^{-7}$		3.3	3.3	2.9	2.5	2.3	2.6	2.4	
	$\text{Ca} \times 10^{-3}$		6.9	6.6	6.5	6.4	5.7	4.9	4.3	
Apatite: Marine (as above)		0	1	5	9	24	72	192		
500	$\text{TPO}_4 \times 10^{-6}$		2.5	0.25	0.25	0.25	0.25	8.5	19.3	
	$\text{F} \times 10^{-3}$		8.2	7.9	8.1	7.7	5.2	3.3	6.4	
	$\text{OH} \times 10^{-7}$		-	1.4	1.3	-	0.77	0.35	0.48	
	$\text{Ca} \times 10^{-3}$		6.0	7.0	6.5	7.4	6.5	6.4	8.0	
Apatite: Florida (as above)		0	3	6	10	24	48	96	192	
500	$\text{TPO}_4 \times 10^{-6}$		-	7.5	2.2	5.5	14	10.3	-	25.8
	$\text{F} \times 10^{-3}$		11.2	7.9	7.7	7.0	8.6	-	-	6.45
	$\text{OH} \times 10^{-7}$		4.6	5.3	3.8	4.5	3.4	3.3	3.2	4.5
	$\text{Ca} \times 10^{-3}$		-	7.3	7.5	7.3	7.1	6.7	7.2	6.9

TABLE B8 (b)

Experiment High-Level Variation in Fluoride, High Temperature

Solution: Seawater + NaF (1 atm., 500 ppm NaF spike)

Apatite. Ontario (8-28 mesh, 5g/100cc)

Temperature (°C)	Conc (M)	Time (Hours)					
		0	2	6	8	24	95
25	$\text{TPO}_4 \times 10^{-6}$	2.1	0.67	1.0	0.3	0.45	-
	$\text{F} \times 10^{-3}$	6.4	7.4	8.1	7.6	5.6	5.0
	$\text{OH} \times 10^{-7}$	1.5	7.1	7.8	6.9	3.3	15.0
	$\text{Ca} \times 10^{-3}$	6.0	6.8	7.45	6.9	7.1	7.1
50	$\text{TPO}_4 \times 10^{-6}$	1.6	1.3	0.9	-	1.1	0.66
	$\text{F} \times 10^{-3}$	6.3	6.5	6.5	6.3	4.6	4.1
	$\text{OH} \times 10^{-6}$	1.7	1.5	1.5	1.5	1.7	1.4
	$\text{Ca} \times 10^{-3}$	6.6	6.9	6.8	6.9	6.8	6.9

TABLE B9

Experiment: Variation of Calcium and Magnesium in Solution
 Solution. Seawater + Art. Seawater (1 atm, 2°C)

Apatite. Ontario (8-28 mesh, 5g/100cc)

Ratio Ca/Mg	Conc (M)	Time (Hours)							
		0	1	3	5	9	24	96	192
2.5	$\text{TPO}_4 \times 10^{-6}$	2.	0.25	0.25	0.25	0.25	2	3.45	7.84
	$\text{F} \times 10^{-5}$	9.3	6.1	5.8	6.1	9.4	6.6	6.9	12.1
	$\text{OH} \times 10^{-8}$	6.8	8.2	9.2	9.6	9.0	7.1	25.	36.
	$\text{Ca} \times 10^{-3}$	9.3	8.0	8.0	8.8	8.9	9.0	11.6	11.0
	$\text{Mg} \times 10^{-3}$	5.1	7.8	7.8	4.95	4.9	4.8	4.8	5.1
5	$\text{TPO}_4 \times 10^{-6}$	2.	0.25	0.25	0.25	0.25	0.98	-	2.91
	$\text{F} \times 10^{-5}$	12.6	9.3	12.8	8.9	11.8	11.0	17.4	12.7
	$\text{OH} \times 10^{-7}$	4.9	4.3	4.8	4.0	4.1	3.4	3.7	4.8
	$\text{Ca} \times 10^{-3}$	9.8	7.65	7.54	8.9	8.1	7.8	11.5	11.3
	$\text{Mg} \times 10^{-3}$	2.7	2.9	1.80	2.4	2.3	2.45	2.5	2.4
10	$\text{TPO}_4 \times 10^{-6}$	2.	0.25	0.25	0.25	0.25	1.8	-	2.12
	$\text{F} \times 10^{-5}$	23.4	14.0	17.0	13.8	15.1	22.9	22.4	81.1
	$\text{OH} \times 10^{-7}$	5.0	4.9	5.3	4.8	4.8	4.2	4.8	3.9
	$\text{Ca} \times 10^{-3}$	9.7	8.1	9.1	9.3	9.1	8.5	11.3	11.8
	$\text{Mg} \times 10^{-3}$	1.3	1.3	1.3	1.45	1.25	1.3	1.45	1.59
		0	1	3	5	8	24	144	192
0.033	$\text{TPO}_4 \times 10^{-5}$	0.25	1.79	1.07	1.43	1.43	3.4	3.2	5.7
	$\text{F} \times 10^{-5}$	5.3	7.7	9.	-	6.	8.1	8.8	14.8
	$\text{OH} \times 10^{-7}$	2.5	2.9	3.0	3.5	3.8	3.8	4.0	2.4
	$\text{Ca} \times 10^{-4}$	8.3	8.85	-	9.3	9.5	11.0	9.5	10.6
	$\text{Mg} \times 10^{-2}$	10.8	11.2	12.3	11.0	10.9	10.1	10.8	10.6
0.0033	$\text{TPO}_4 \times 10^{-5}$.025	0.91	1.72	1.8	1.55	2.15	6.5	6.6
	$\text{F} \times 10^{-5}$	5.3	6.2	7.6	6.5	6.9	8.1	9.5	13.6
	$\text{OH} \times 10^{-7}$	2.5	2.9	3.1	3.5	4.1	4.2	4.7	3.9
	$\text{Ca} \times 10^{-4}$	0.9	1.0	1.6	2.4	2.1	3.6	3.6	3.9
	$\text{Mg} \times 10^{-2}$	11.0	10.3	10.5	10.2	10.1	10.4	9.9	10.4

TABLE B10

Experiment Variation of Total CO_2 in Solution
 Solution. Seawater + K_2CO_3 or HCl (1 atm, 2°C)

Apatite Mexico (8-28 mesh, 50g/1000cc)

TCO ₂	Conc (M)	Time (Hours)							
		0	2	6	10	24	48	145	192
High	$\text{TPO}_4 \times 10^{-5}$	0.057	9.9	21.1	25.1	34.4	21	18.1	14
	$\text{F} \times 10^{-5}$	2.8	4.0	3.8	4.5	8.0	12.0	-	24
	$\text{OH} \times 10^{-6}$	28	8.2	4.7	0.02	0.06	1.1	3.0	2
	$\text{Ca} \times 10^{-3}$	5.8	6.6	5.2	6.6	6.9	8.7	6.4	6.9
	$\text{TCO}_2 \times 10^{-3}$	1.22	3.96	4.05	-	4.9	-	4.5	4.6
Regular	$\text{TPO}_4 \times 10^{-4}$	0.02	1.1	2.05	2.3	2.6	2.0	3.8	3.4
	$\text{F} \times 10^{-5}$	2	4.1	3.4	3.8	5.6	7.7	15.1	11.5
	$\text{OH} \times 10^{-3}$	7.8	0.3	1.0	2.0	0.67	2.6	1.2	8.9
	$\text{Ca} \times 10^{-3}$	9.0	8.1	6.8	8.8	8.8	9.3	7.0	6.8
	$\text{TCO}_2 \times 10^{-3}$	-	-	2.1	-	-	-	2.2	2.2
Low	$\text{TPO}_4 \times 10^{-4}$	0.07	1.85	2.7	3.4	3.5	2.5	4.6	4.4
	$\text{F} \times 10^{-5}$	1.7	5.8	4.8	5.1	6.7	9.4	18.6	14.0
	$\text{OH} \times 10^{-7}$	0.0004	0.002	0.04	0.08	0.41	5.4	12.	7.7
	$\text{Ca} \times 10^{-3}$	8.2	9	8.9	7.9	8.3	9.9	6.0	7.1
	$\text{TCO}_2 \times 10^{-3}$	0.89	0.49	-	-	-	0.02	0.15	0.46

Apatite Ontario (as above)

High	$\text{TPO}_4 \times 10^{-5}$	0.06	9.6	18.8	22.3	29.5	21.3	30.6	21.0
	$\text{F} \times 10^{-5}$	2.3	4.1	3.9	4.7	9.8	14.0	51.1	36.0
	$\text{OH} \times 10^{-6}$	28	6.5	2.2	0.01	0.04	0.92	2.3	2.1
	$\text{Ca} \times 10^{-3}$	5.8	7.8	7.8	7.8	7.3	8.3	7.9	6.7
	$\text{TCO}_2 \times 10^{-3}$	1.2	4.7	6.0	-	6.3	6.4	5.9	6.0
Regular	$\text{TPO}_4 \times 10^{-5}$	0.06	10.7	20.2	20.3	16.3	-	17.8	17.4
	$\text{F} \times 10^{-5}$	2.0	4.3	4.1	4.5	5.9	8.5	39.4	24.2
	$\text{OH} \times 10^{-7}$	7.8	0.54	1.6	2.1	0.73	1.75	2.3	9.2
	$\text{Ca} \times 10^{-3}$	8.1	9.0	7.3	9.6	8.0	8.0	6.6	6.6
	$\text{TCO}_2 \times 10^{-3}$	-	-	2.4	-	-	2.3	-	2.4
Low	$\text{TPO}_4 \times 10^{-5}$	0.07	10.1	20.	21.2	22.5	-	15.0	13.0
	$\text{F} \times 10^{-5}$	1.7	5.0	4.6	5.2	6.9	8.9	-	13.9
	$\text{OH} \times 10^{-7}$	0.0003	0.01	0.09	0.05	0.5	2.2	-	7.8
	$\text{Ca} \times 10^{-3}$	8.2	8.9	7.4	10.1	8.9	9.2	6.7	5.8
	$\text{TCO}_2 \times 10^{-3}$	0.89	0.64	0.24	-	0.46	0.67	0.80	0.83

TABLE B11

Experiment Regular, Seawater with Apatite Pretreated in Seawater
(1 atm., 2°C) for Various Lengths of Time

Solution Seawater (1 atm., 2°C)

Apatite Mexico (8-28 mesh, 5 g/100cc)

Pretreatment Time (Hr)	Conc (M)	Time (Hours)					
		2	6	10	24	96	192
192	$\text{TPO}_4 \times 10^{-6}$	4.7	3.9	6.1	6.0	11.9	17.3
	$\text{F} \times 10^{-5}$	3.6	3.6	4.1	3.6	3.6	8.6
	$\text{OH} \times 10^{-7}$	4.3	5.2	5.2	4.3	4.6	4.9
	$\text{Ca} \times 10^{-3}$	6.0	6.1	7.7	5.7	5.9	8.2
384	$\text{TPO}_4 \times 10^{-6}$	1.6	2.8	9.0	5.3	9.7	31.9
	$\text{F} \times 10^{-5}$	9.5	5.1	4.7	3.6	-	11.6
	$\text{OH} \times 10^{-7}$	5.7	5.7	5.4	5.8	5.4	4.2
	$\text{Ca} \times 10^{-3}$	5.5	6.6	8.2	5.9	5.6	7.3

Apatite: Florida (as above)

192	$\text{TPO}_4 \times 10^{-6}$	4.9	5.3	8.2	-	11.6	11.7
	$\text{F} \times 10^{-5}$	3.4	4.0	4.7	2.4	-	5.6
	$\text{OH} \times 10^{-7}$	4.6	4.2	4.1	3.9	3.8	4.1
	$\text{Ca} \times 10^{-3}$	5.9	8.8	7.4	5.4	7.2	8.3
384	$\text{TPO}_4 \times 10^{-6}$	-	-	1.3	2.5	13.8	16.5
	$\text{F} \times 10^{-5}$	3.5	2.9	4.7	-	-	8.5
	$\text{OH} \times 10^{-7}$	5.4	4.4	4.9	4.6	4.1	3.7
	$\text{Ca} \times 10^{-3}$	6.3	6.2	8.0	5.5	6.5	7.3

Apatite: Marine (10g/100cc, as above)

192	$\text{TPO}_4 \times 10^{-6}$	5	4.2	12.7	-	-	10.4
	$\text{F} \times 10^{-5}$	8.5	3.6	4.4	10.2	10.0	12.7
	$\text{OH} \times 10^{-8}$	13.	8.4	5.9	3.1	1.5	1.4
	$\text{Ca} \times 10^{-3}$	5.9	6.5	8.2	6.8	6.3	8.2
384	$\text{TPO}_4 \times 10^{-6}$	2.7	4.3	1.2	20.4	-	11.9
	$\text{F} \times 10^{-5}$	20.4	-	-	10.2	10.5	8.9
	$\text{OH} \times 10^{-8}$	23.	13.	13.	1.3	1.0	0.94
	$\text{Ca} \times 10^{-3}$	5.8	6.2	8.0	6.2	6.6	11.1

TABLE B12

Experiment: Regular Seawater with Apatite Pretreated in Seawater
+ K_2HPO_4 for 192 Hr, 2°, 1 atm.

Solution: Seawater (1 atm., 2°C)

Apatite Mexico (8-28 mesh, 5g/100cc)

Pretreated in SW + - (M) K_2HPO_4	Conc (M)	Time (Hours)					
		0	2	6	10	24	96 192
25×10^{-6}	$TPO_4 \times 10^{-6}$		3.5	3.3	3.6	5.5	4.4 3.4
	F $\times 10^{-5}$		3.8	3.7	4.2	3.4	3.3 4.5
	OH $\times 10^{-7}$		4.2	4.5	4.5	4.3	4.2 4.8
	Ca $\times 10^{-3}$		6.1	5.8	7.0	6.0	5.7 7.1
50×10^{-6}	$TPO_4 \times 10^{-6}$		6.5	3.8	5.6	6.0	4.7 29.
	F $\times 10^{-5}$		3.5	3.8	4.2	3.6	3.8 3.8
	OH $\times 10^{-7}$		3.8	4.5	4.5	4.3	4.2 5.1
	Ca $\times 10^{-3}$		5.8	-	8.0	6.6	7.0 7.2

Apatite Florida (as above)

25×10^{-6}	$TPO_4 \times 10^{-6}$		7.0	7.7	11.3	-	19.2
	F $\times 10^{-5}$		3.5	3.8	4.8	2.2	5.8
	OH $\times 10^{-7}$		4.2	3.8	3.8	3.6	4.4
	Ca $\times 10^{-3}$		5.9	6.4	8.3	7.0	7.8
50×10^{-6}	$TPO_4 \times 10^{-5}$		1.2	1.1	1.3	-	2.6
	F $\times 10^{-5}$		3.7	3.9	4.4	2.6	5.6
	OH $\times 10^{-7}$		4.2	3.7	3.6	3.5	4.0
	Ca $\times 10^{-3}$		12.2	8.3	4.6	6.8	7.8

TABLE B13

Experiment. Regular Seawater with Apatite Pretreated in Seawater
+ NaF (500 ppm) for 192 Hr., 1 atm., 2°C.

Solution. Seawater (1 atm., 2°C).

Apatite: Mexico (8-28 mesh, 5g/100cc)

Conc. (M)	Time (Hours)						
	0	2	6	10	24	96	192
$\text{TPo}_4 \times 10^{-6}$		0.25	0.25	0.25	0.25	0.64	1.22
$\text{F} \times 10^{-3}$		1.26	1.20	1.46	1.6	2.5	2.5
$\text{OH} \times 10^{-7}$		4.1	4.1	4.1	4.1	3.9	3.7
$\text{Ca} \times 10^{-3}$		6.7	5.4	8.4	6.1	-	8.6

Apatite. Ontario (as above)

$\text{TPo}_4 \times 10^{-6}$	0.25	0.25	0.25	0.25	0.25	2.4
$\text{F} \times 10^{-3}$	0.87	1.3	-	1.84	2.45	2.5
$\text{OH} \times 10^{-7}$	4.4	4.4	4.4	5.3	5.2	4.5
$\text{Ca} \times 10^{-3}$	6.1	6.5	7.9	7.0	7.4	8.4