

AD 716049

TITLE: GEOCHEMISTRY OF THE CARBONATE CYCLE IN THE MARINE ENVIRONMENT

AUTHOR: Keith E. Chave  
Professor of Oceanography  
University of Hawaii  
Honolulu, Hawaii 96822

DATE OF ISSUE: December 28, 1970

REPORT NUMBER: Final Report

CONTRACTOR: University of Hawaii

ONR CONTRACT NUMBER: N00014-67-A-0387-0002

TASK NUMBER: NR 083-194

Reproduction in whole or in part is permitted for any purpose of the United States Government.

Distribution of this document is unlimited.

Approved and for  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
Springfield, Va. 22151

DDC  
RECEIVED  
JAN 1 1971  
REGISTERED  
B

... ..  
... ..  
... ..

6

## GEOCHEMISTRY OF THE CARBONATE CYCLE IN THE MARINE ENVIRONMENT

### General Statement:

This final report is relatively short because most of the results have been published and distributed.

The carbonate cycle in the marine environment is characterized by very slow reaction rates and chemical disequilibrium (Chave and Smith, in press). The cycle involves atmospheric  $\text{CO}_2$ , dissolved calcium and carbon ions and complexes, suspended mineral particles, sediments, and living organisms. Our contribution to the understanding of the slow reaction rates in this cycle has been the demonstration that organic compounds in seawater are a major factor regulating reaction rates (Chave, 1965; Chave and Suess, 1967; Suess, 1968; Suess, 1970; Chave and Suess, 1970).

### U.S. Navy Relevance:

#### 1. Sediment distribution patterns.

The slowness of the reaction rates involving carbonates in the ocean prevents simple prediction of sediment distribution patterns on the basis of chemical thermodynamics. Carbonate sediments exist on the deep sea floor where waters are undersaturated with respect to  $\text{CaCO}_3$  (Smith, Dygas and Chave, 1968), yet carbonates dissolve in relatively shallow water associated with the  $\text{O}_2$ -minimum (Smith, 1970).

These observations, plus the fact that carbonate sediments occur, not only in the tropics, but at all latitudes (Chave, 1967), have led us to our present study of reaction rates on the deep sea floor, and the effects of these reactions on acoustical and other physical properties of the sediments (N00014-70-A-0016-0001; Nr 083-603; Task 3).

## 2. Interfaces.

Our studies of reactions of organic materials at the carbonate mineral-seawater interface suggest that similar reactions may be taking place at other--U.S. Navy relevant--interfaces, such as the air-sea interface, instrument package-sea interface, and the ship-sea interface. Work at the Navy Research Laboratory in Washington, by Garrett and others (Garrett, 1967, for instance) has shown that the same organic compounds that are absorbed to carbonate mineral grains in the ocean are absorbed to the air-sea interface, modifying the physical properties of this interface as well. The same could certainly be true of other interfaces in the ocean.

## 3. Scale formation.

Near-surface seawater is chemically unstable, reaching more than 700% supersaturation with respect to  $\text{CaCO}_3$  (Lyakhin, 1968). Although these waters do not precipitate their excess  $\text{CaCO}_3$  spontaneously, largely as a result of interactions with dissolved organic matter in sea-water (Chave and Suess, 1970), when physically disturbed, for instance by heating or by passing through a small orifice the carbonate precipitates out as scale. A thorough understanding of the organic chemistry of this precipitation inhibition could lead to the solution of problems of scale formation.

### Personnel and Publications:

The two principal workers on this contract, other than the principal investigator, have received Ph.D. degrees: Erwin Suess (1968) and Stephen V. Smith (1970). A majority of the references listed below were supported by this contract and have been, or will be, distributed to the Navy distribution list.

References:

- Chave, K.E. 1965. Calcium carbonate: Association with organic matter in surface seawater. *Science* 148, 1723-1724.
- \_\_\_\_\_ 1967. Recent carbonate sediments--An unconventional view. *J. Geol. Ed.* 15, 200-204.
- \_\_\_\_\_, and S. V. Smith. in press. Inorganic cycles of calcium and carbon in the ocean. 1970 International Symposium on Hydrogeochemistry and Biogeochemistry, Tokyo, Pergamon Press.
- \_\_\_\_\_, and E. Suess. 1967. Suspended minerals in seawater. *Trans. N. Y. Acad. Sci.* 31, 29, 991-1000.
- \_\_\_\_\_, and E. Suess. 1970. Calcium carbonate saturation in seawater: Effects of dissolved organic matter. *Limnol. and Oceanogr.* 15, 633-637.
- Garrett, W.D. 1967. The organic chemical composition of the ocean surface. *Deep sea Res.* 14, 221-227.
- Lyahkin, Y.I. 1968. Calcium carbonate saturation of Pacific water. *Oceanology (Translation)* 8, 44-53.
- Smith, S.V. 1970. Calcium carbonate budget of the Southern California Borderland. Ph.D. Thesis, University of Hawaii, HIG Report 70-11, 174 p.
- \_\_\_\_\_, J.A. Dygas and K.E. Chave, 1968. Distribution of calcium carbonate in pelagic sediments. *Mar. Geol.* 6, 391-400.
- Suess, E. 1968. Calcium carbonate interaction with organic compounds. Ph.D. Thesis, Lchigh University, 1-3 p.
- \_\_\_\_\_ 1970. Interaction of organic compounds with calcium carbonate--I. Association phenomena and Geochemical implications. *Geochim Cosmochim Acta* 34, 157-168.

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Hawaii Institute of Geophysics University of Hawaii Honolulu, Hawaii 96822		2a. REPORT SECURITY CLASSIFICATION none	
		2b. GROUP none	
3. REPORT TITLE Geochemistry of the Carbonate Cycle in the Marine Environment			
4. DESCRIPTIVE NOTES (Type of report and Inclusive dates) Final Report			
5. AUTHOR(S) (Last name, first name, initial) Chave, Keith E.			
6. REPORT DATE 28 December 1970	7a. TOTAL NO. OF PAGES 3	7b. NO. OF REFS 11	
8a. CONTRACT OR GRANT NO. N 00014-67-A-0387-0002	9a. ORIGINATOR'S REPORT NUMBER(S) None		
b. PROJECT NO. NR 083-194	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) None		
c.			
d.			
10. AVAILABILITY/LIMITATION NOTICES Unlimited			
11. SUPPLEMENTARY NOTES None		12. SPONSORING MILITARY ACTIVITY Department of the Navy Office of Naval Research, Ocean Science and Technology Division Arlington, Virginia 22217	
13. ABSTRACT The carbonate cycle in the marine environment is characterized by very slow reaction rates and chemical disequilibrium (Chave and Smith, in press). The cycle involves atmospheric CO <sub>2</sub> , dissolved calcium and carbon ions and complexes, suspended mineral particles, sediments, and living organisms. Our contribution to the understanding of the slow reaction rates in this cycle has been the demonstration that organic compounds in seawater are a major factor regulating reaction rates. (Chave, 1965; Chave and Suess, 1967; Suess, 1968; Suess, 1970; Chave and Suess, 1970).  <i>The report summarizes the authors.</i>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
U.S. Navy Relevance 1. Sediment distribution patterns 2. Interfaces 3. Scale Formation						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parentheses immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.