

University of Montana

## ScholarWorks at University of Montana

---

Graduate Student Theses, Dissertations, &  
Professional Papers

Graduate School

---

1977

### Diagenesis of the Lower Ordovician Manitou Formation El Paso County Colorado

John R. Forster  
*The University of Montana*

Follow this and additional works at: <https://scholarworks.umt.edu/etd>

**Let us know how access to this document benefits you.**

---

#### Recommended Citation

Forster, John R., "Diagenesis of the Lower Ordovician Manitou Formation El Paso County Colorado" (1977). *Graduate Student Theses, Dissertations, & Professional Papers*. 7727.  
<https://scholarworks.umt.edu/etd/7727>

This Thesis is brought to you for free and open access by the Graduate School at ScholarWorks at University of Montana. It has been accepted for inclusion in Graduate Student Theses, Dissertations, & Professional Papers by an authorized administrator of ScholarWorks at University of Montana. For more information, please contact [scholarworks@mso.umt.edu](mailto:scholarworks@mso.umt.edu).

DIAGENESIS OF THE LOWER ORDOVICIAN MANITOU FORMATION,  
EL PASO COUNTY, COLORADO

by

John R. Forster

B.A., The Colorado College, 1975

Presented in partial fulfillment of the  
requirements for the degree of

Master of Science

UNIVERSITY OF MONTANA

1977

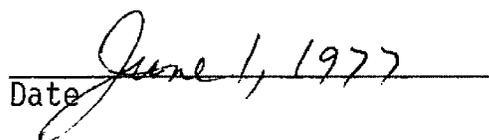
Approved by:



Chairman, Board of Examiners



Dean, Graduate School



Date

UMI Number: EP38528

All rights reserved

**INFORMATION TO ALL USERS**

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI EP38528

Published by ProQuest LLC (2013). Copyright in the Dissertation held by the Author.

Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code



ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 - 1346

ABSTRACT

Forster, John R., M.S., Spring, 1977

Geology

Diagenesis of the Lower Ordovician Manitou Formation, El Paso County, Colorado (113 p.)

Director: Don Winston



West of Manitou Springs, El Paso County, Colorado, the Lower Ordovician Manitou Formation is well exposed at two geologically distinct localities: 1) Williams Canyon where relatively unaltered rocks are gray limestone and buff dolomite with limited numbers of bedded white chert nodules; and 2) Indian Trail along the Ute Pass Fault Zone, where the rocks are strongly altered red dolomite with abundant beds and nodules of white chert.

Bed by bed correlation of measured sections at both localities enabled comparison of the original sediment and a detailed petrologic comparison of the diagenesis. Seven major diagenetic episodes can be distinguished: E-1 Cementation; E-2 Solution; E-3 Dolomitization; E-4 Silicification; E-5 Dolomitization; E-6 Weathering; and E-7 Calcitization. E-6 consisted of three processes 6a-dolomitization; 6b-silicification and 6c-solution. Episodes one through five took place in a similar way at both localities because as the rocks were deposited they went through a series of diagenetic changes. This conclusion differs from traditional interpretations of diagenesis because instead of separating each diagenetic event into time intervals, I believe the events overlapped in time and the sequence results from the passage of sediments through a series of diagenetic environments which were simultaneously acting on the rocks. These episodes were followed by subaerial exposure and deep weathering at the Indian Trail Locality during the post-Manitou pre-Devonian Williams Canyon limestone hiatus, creating red dolomite with abundant beds of white chert and karst collapse breccias. The Dorag model of dolomitization by mixing saline and fresh waters explains the E-6 dolomitization and is extended to include the E-6 silicification and formation of karst breccias. Weathering was followed by calcitization at both localities.

## ACKNOWLEDGMENTS

Thanks go to Dr. Dave Alt, Dr. Ray Murray, Dr. Keith Osterheld and Shirley Pettersen for their guidance in this project. Special thanks go to Dr. Don Winston for the many hours spent in preparation of this manuscript and for his monies spent in visiting the field area. This project would never have been completed without the aid of my wife, Pam, who cheerfully typed the many drafts for editing. Field work was supported in part by a Grant-in-Aid of Research from the Society of Sigma Xi.

## TABLE OF CONTENTS

	Page
ABSTRACT . . . . .	ii
ACKNOWLEDGMENTS . . . . .	iii
LIST OF FIGURES . . . . .	vi
CHAPTER	
I. INTRODUCTION . . . . .	1
General Statement . . . . .	1
Physical and Stratigraphic Location . . . . .	2
Statement of Problem . . . . .	2
II. DEPOSITION AND CORRELATION . . . . .	9
General Statement . . . . .	9
Unit I . . . . .	9
Unit II . . . . .	10
Unit III . . . . .	15
III. DIAGENESIS . . . . .	17
General Statement . . . . .	17
Episode 1 - Cementation . . . . .	17
Episode 2 - Solution . . . . .	26
Episode 3 - Dolomitization . . . . .	33
Episode 4 - Silicification . . . . .	33
Episode 5 - Dolomitization . . . . .	43
Episode 6 - Weathering . . . . .	46

## TABLE OF CONTENTS (Continued)

CHAPTER	Page
Dolomitization - E-6a . . . . .	48
Silicification - E-6b . . . . .	52
Solution - E-6c . . . . .	58
Discussion - Episode 6 . . . . .	59
Episode 7 - Calcitization . . . . .	65
Summary of Diagenesis . . . . .	68
E-1 Cementation . . . . .	68
E-2 Solution . . . . .	68
E-3 Dolomitization . . . . .	72
E-4 Silicification . . . . .	72
E-5 Dolomitization . . . . .	72
E-6 Weathering . . . . .	72
Dolomitization - 6a . . . . .	72
Silicification - 6b . . . . .	73
Solution - 6c . . . . .	73
E-7 Calcitization . . . . .	73
Discussion . . . . .	73
IV. SUMMARY AND CONCLUSIONS . . . . .	80
REFERENCES CITED . . . . .	84
APPENDIX I. Measured Sections . . . . .	87
APPENDIX II. Correlation of Measured Sections . . . . .	112

## LIST OF FIGURES

Figure	Page
1. Geologic Map of Study Area . . . . .	3
2. Localities and measured section localities . . . . .	6
3. Thin bedded limestone . . . . .	11
4. Daisycladacean Algae . . . . .	14
5. Lacy limestone . . . . .	14
6. Hardgrounds . . . . .	20
7. Thin bedded limestone . . . . .	23
8. Thin bedded limestone . . . . .	25
9. Lacy limestone cut by scour surfaces . . . . .	32
10. Silicified trilobite fragment in micrite . . . . .	35
11. Partially dolomitized and silicified trilobite fragments in micrite . . . . .	35
12. Silicified calcareous sponge spicules . . . . .	38
13. Eh-pH diagram for iron . . . . .	42
14. Solubility curves for quartz, amorphous silica, and calcite . . . . .	42
15. Calcite cement with later silica cement . . . . .	45
16. Silicified micrite intraclasts . . . . .	45
17. Clotted red iron on dolomite rhombs . . . . .	51
18. Silica-dolomite boundary . . . . .	51
19. Composite chert nodules . . . . .	54
20. Silicified intraclasts replaced by calcite . . . . .	56
21. Silicified dolomite rhombs . . . . .	56

LIST OF FIGURES (Continued)

Figure		Page
22.	Solubility curve for calcite . . . . .	61
23.	Solubility curve for amorphous silica . . . . .	61
24.	Mixing of 5-30% sea water with fresh water causes dolomitization . . . . .	64
25.	Weathering model . . . . .	67
26.	Calcite truncating silica-micrite boundary . . . . .	69
27.	Calcite replacing dolomite . . . . .	71
28.	Calcite - Silica - Micrite Relationship . . . . .	71
29.	Time relationship of diagenetic episodes . . . . .	77

CHAPTER I  
INTRODUCTION

General Statement

The diagenetic formation of dolomite and chert in limestone has been studied by a great many geologists, (Walker, 1963; Friedman, 1964; Banks, 1967; Roehl, 1967, and many more) but many problems of diagenetic sequence and processes still remain unsolved. Dolomitization and silicification of lime sediments in the extensive Lower Ordovician rocks have been particularly perplexing (Cloud and Barnes, 1957). The Manitou Formation, El Paso County, Colorado, offers an exceptionally good opportunity to further study the diagenesis of a Lower Ordovician limestone. Swett (1964) proposed a probable sequence of diagenetic mineral formation for the Manitou Limestone but was unable to establish a detailed stratigraphic framework for accurate correlation of the relatively unaltered sections and the pervasively dolomitized and silicified sections, thus limiting his study to proposing a probable sequence of diagenetic mineral formation. I have been able to correlate a relatively unaltered section with a strongly altered section. Study of the diagenesis on a unit by unit basis has allowed me to revise Swett's (1964) work and possibly better understand some of the diagenetic sequences and processes.

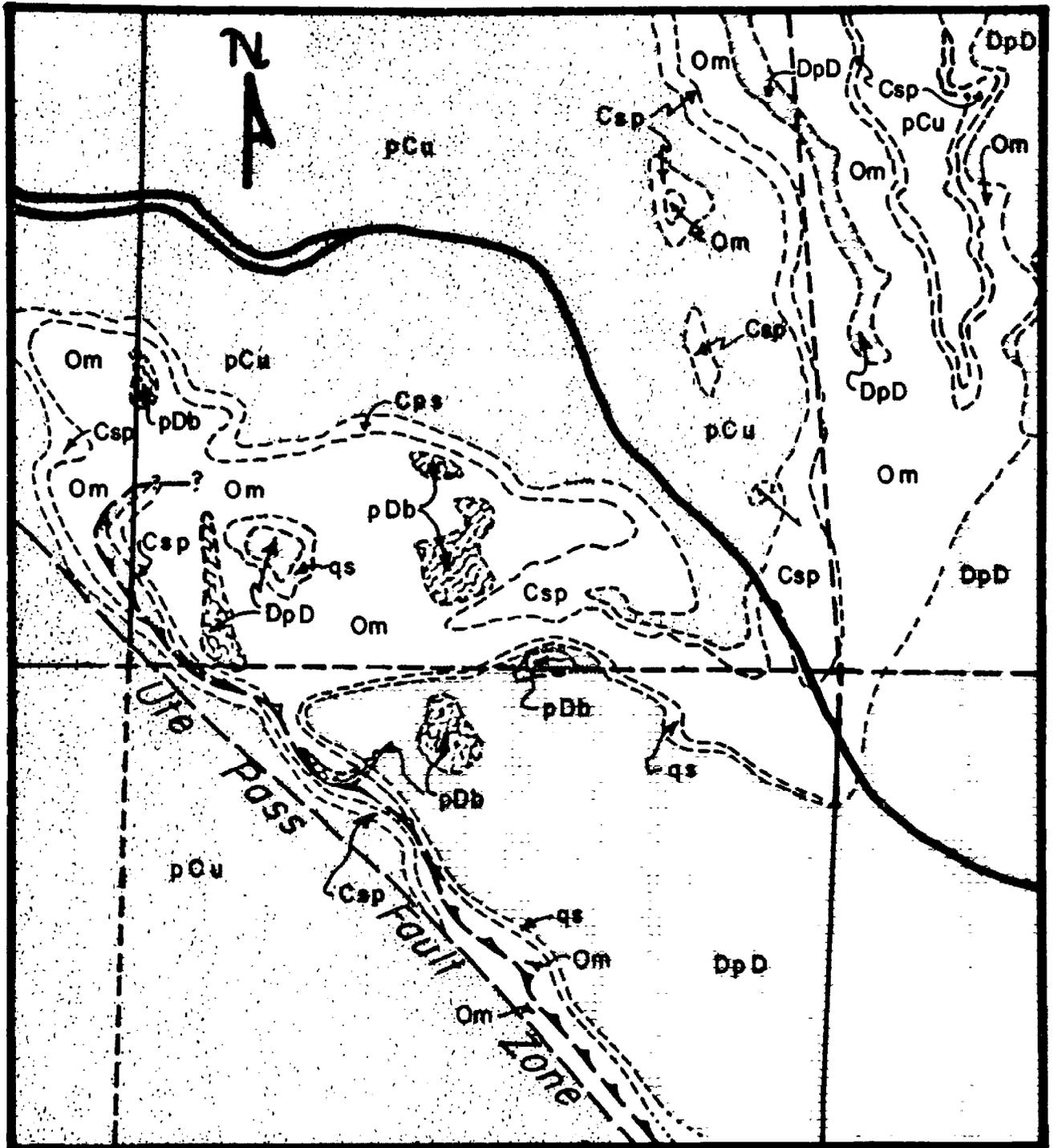
### Physical and Stratigraphic Location

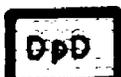
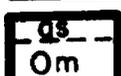
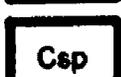
West of Manitou Springs, El Paso County, Colorado, the Lower Ordovician Manitou Limestone is well exposed in sec. 6; T.14S.; R.67W. and secs. 31 and 32; T.13S.; T.67W. This area can be divided into two distinct geologic localities (Fig. 1 and 2); (1) The area southwest of U.S. Highway 24, hereafter referred to as the Indian Trail Locality; (2) The area northeast of U.S. Highway 24, known as Williams Canyon. The Manitou Limestone was deposited over the eroded Cambrian Peerless Formation at both localities. Overlying the Manitou Limestone at the Indian Trail Locality is a quartzite unit of unknown age, possibly the Middle Ordovician Harding Formation. At Williams Canyon the Manitou Limestone is overlain by the Devonian Williams Canyon Limestone (Maher, 1950).

### Statement of Problem

Indian Trail and Williams Canyon represent two geologically distinct localities (Fig. 2). At Williams Canyon, the Manitou Limestone is a buff or gray limestone with a minor amount of dolomite and has undergone little diagenetic alteration. Abundant spicular chert nodules occur at only occasional horizons. The Indian Trail area, 1.2 km (1.5 miles) southwest of Williams Canyon, lies adjacent to the Ute Pass Fault Zone. Here the Manitou Limestone is pervasively dolomitized (except in the basal 8.6 meters), red and brown in color, and has abundant chert nodules and beds.

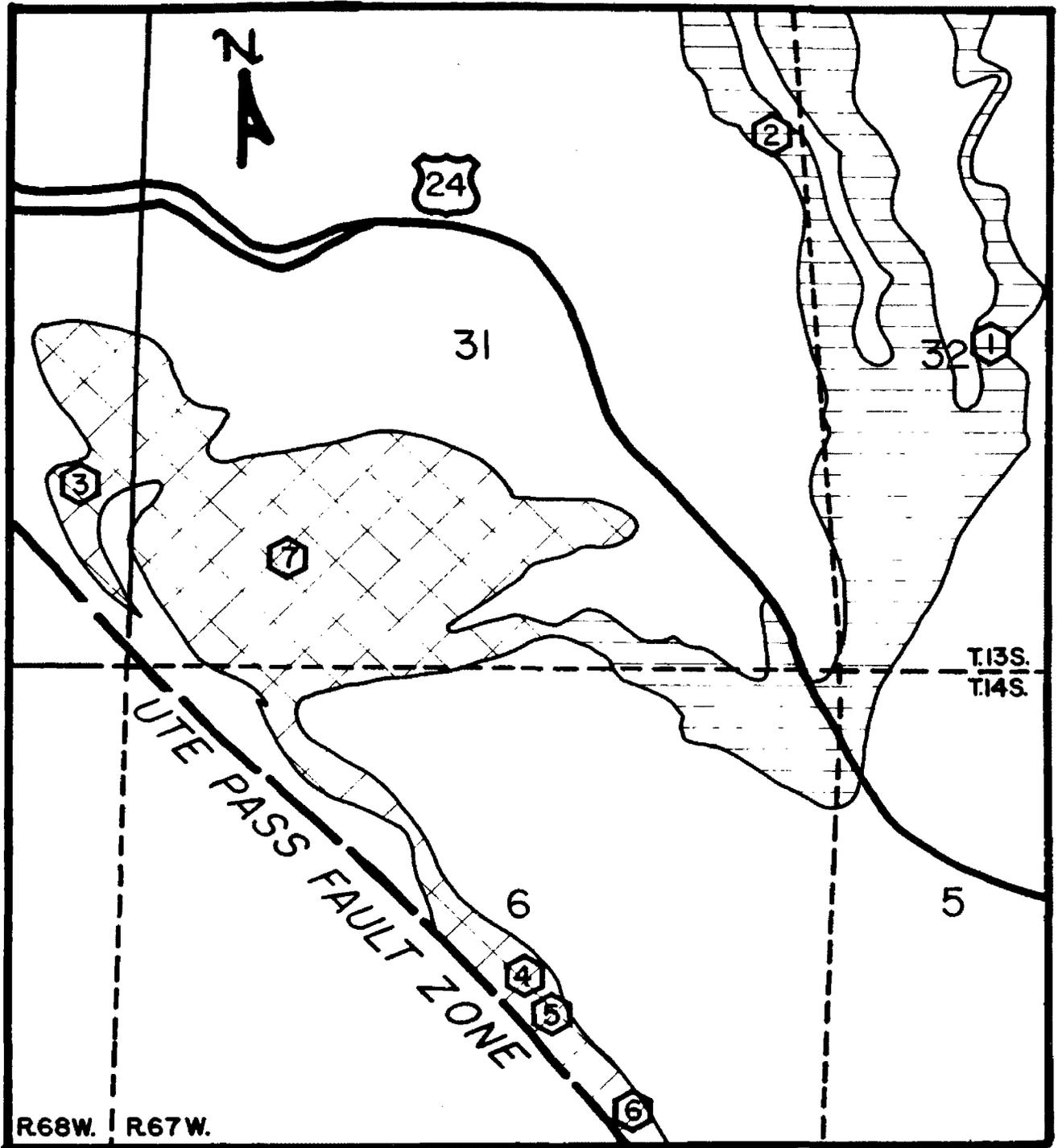
Figure 1. Geologic Map of Study Area



-  post Devonian solution breccia
-  Devonian and post Devonian limestone and arkose
-  Ordovician Manitou Fm. and over lying quartz siltstone
-  Cambrian Sawatch and Peerless undifferentiated
-  pre Cambrian undifferentiated

0 FEET 2000

Figure 2. Map showing the two geologically distinct areas and locations of measured sections.



-  WILLIAMS CANYON LOCALITY
-  INDIAN TRAIL LOCALITY
-  MEASURED SECTION LOCATIONS



Swett (1964) in a similar way, distinguished two lithologies of the Manitou: (1) pervasively dolomitized rocks which outcrop to the south of the Manitou Springs area at Deadmans Canyon, Oil Creek, and Phantom Canyon; and (2) the relatively unaltered limestones at Williams Canyon, and to the north of the Manitou Springs area at The Air Force Academy. The sections at Indian Trail are similar in most aspects to the dolomitized southern localities studied by Swett (1964) and are close enough to the sections in Williams Canyon to be correlated on a unit by unit basis. Swett (1964) did not correlate between the southern localities and Williams Canyon because dolomitization was too complete.

A probable paragenesis for the Manitou was proposed by Swett (1964) as follows: (1) Deposition, largely as an organic allochemical limestone with up to 15 percent rock fragments of chert and orthoquartzite; (2) Neomorphic recrystallization of micrite to microsparite; (3) Dolomitization of selected horizons in the northern localities and rather complete dolomitization in the more southern localities. Limestones with a high iron content were selectively dolomitized; (4) Silicification ranging in degree from partial void filling to complete silicification that produced dense chert beds; (5) Calcitization of chert and dolomite; (6) Oxidation of iron bearing minerals, especially glauconite and ankeritic dolomite to limonite and hematite.

I believe a minimum of two major episodes of dolomitization can be distinguished: (1) an early porosity controlled dolomite which is found at both localities; and (2) a pervasive dolomitization at Indian Trail which was the result of weathering. Early silicification present as spicular chert nodules occurs at both localities. A second period of silicification at the Indian Trail Locality is suggested by chert beds and larger nodules with spicular chert centers. The differences between the two localities are possibly the result of a Middle to Upper Ordovician subaerial weathering along the Ute Pass Fault Zone.

## CHAPTER II

### DEPOSITION AND CORRELATION

#### General Statement

Before discussing the diagenesis which changed the rocks of the Manitou Formation it is necessary to interpret what the original carbonate sediments were like compositionally and texturally as they were deposited and to describe what the rocks are now at both localities. The best evidence of the original composition of the sediment is found at Williams Canyon (Sections 1 and 2) where the least post-depositional change has taken place. There I subdivided the section into three units which can be correlated throughout the study area. General unit correlations are presented in the following discussion and more detailed interval by interval correlations are included in Appendix II.

#### Unit I

The basal unit, Unit I, is represented by 0-15 meters (0-49') section 1, 2.1-17.5 meters (7-57') section 3 and 0-7.4 meters (0-24') section 5 (Appendix I). This unit is typically a thin bedded gray and buff limestone (Fig. 3) with occasional intra-clastic packstone beds and lenses up to 30 cm. (12") thick which cannot be correlated between sections. Varying amounts of chert

in all sections occur mostly as interstitial fillings in fossiliferous grainstone beds.

Variations from the typical gray thin bedded limestone of this unit are found from 8.6-17.6 meters (28-57') section 3 and from 0-7.4 meters (0-24') section 5. At these intervals the thin bedded limestones are pervasively dolomitized and stained red by oxidation of iron minerals. Chert nodules which delineate bedding are common in these intervals at both sections 3 and 5, whereas they are sparse at section 1.

Before diagenetic alteration of Unit I, the sediments at the mud-water interface consisted mostly of mudstone with occasional beds of grainstone and packstone. The allochemical constituents in the grainstones and packstones are, in order of decreasing abundance, intraclasts, peloids, sponge spicules, trilobite fragments, daisycladacean algae, and brachiopod fragments. The daisycladacean algae are thread-like structures of radiating calcite from a central core (Fig. 4). The micrite mud was the most dominant sediment, with occasional episodes forming packstones and grainstones, probably during storms.

## Unit II

The middle unit, Unit II, is represented by 15.1-42.1 meters (49-137') section 1, 0-13.5 meters (0-44') section 2, 17.6-42.1 meters

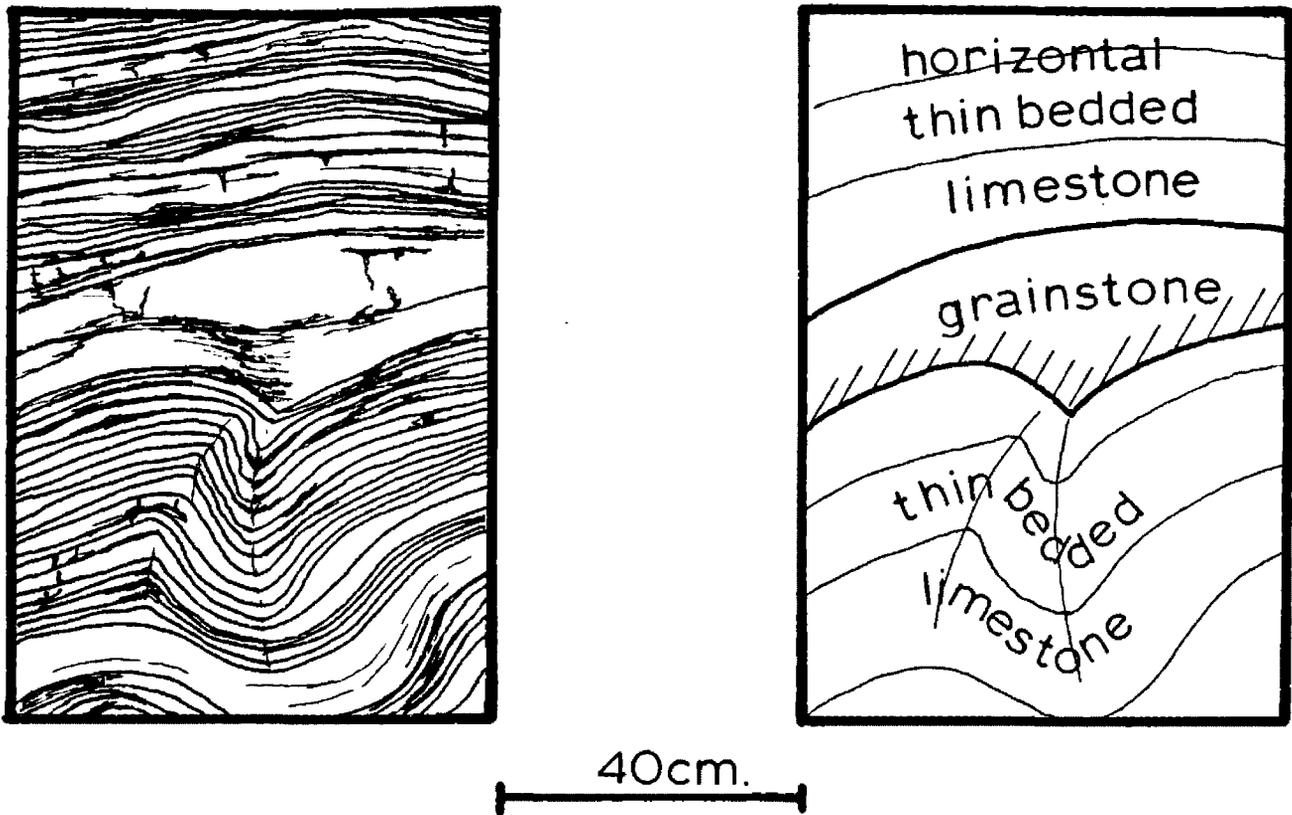


FIGURE 3a

FIGURE 3b

**FIGURE**      **Folded thin bedded limestone overlain by a 30cm. thick grainstone bed and horizontal thin bedded limestone. The folding occurred after solution of the lower micrite and before deposition and solution of the overlying beds. Therefore the solution occurred at or near the mud water interface.**

(57-137') section 3, and 0-22.1 meters (0-72') section 4 (Appendix I). This unit is characterized by abundant beds and nodules of chert in partially dolomitized, massive, gray and buff, thin bedded and nodular limestones. The nodular and thin bedded limestones differ somewhat from the basal thin bedded limestones in that the definite bedding in Unit I is not so dominant in Unit II. In this unit solution resulted in small nodules of gray limestone (less than 2 cm across) separated by lacy whisps of buff dolomite. This type of limestone is herein termed lacy limestone (Fig. 5). Thin bedded limestones which typify Unit I occur only in a few horizons in this unit.

This unit in sections 4 and 5 varies from the typical Unit II in sections 1 and 2 because those sections are pervasively dolomitized and are red and brown instead of gray. In some places both primary depositional features as well as solution and related early diagenetic structures can be seen as ghost structures through this pervasive dolomitization.

At the mud-water interface Unit II was deposited as mudstone, grainstone, and packstone similar to Unit I. However, the amount of mudstone is reduced and the grainstone and packstone beds are more abundant. The allochemical constituents in this unit consist of fewer intraclasts and more sponge spicules, daisycladacean algae, brachiopod fragments and algal stromatolites.

Figure 4. Daisycladacean Algae (?) - Calcite crystals radiating from a micrite core. These are thread-like structures which are up to 1mm in length.

Figure 5. Lacy Limestone - The solution lines are commonly dolomitic, probably due to dolomitizing solutions following the lines of solution.

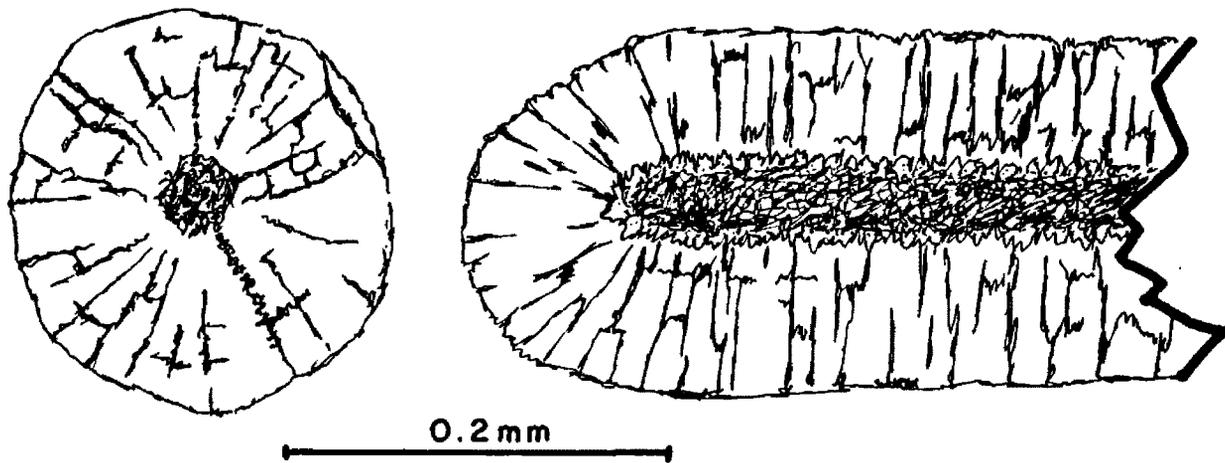


FIGURE 4

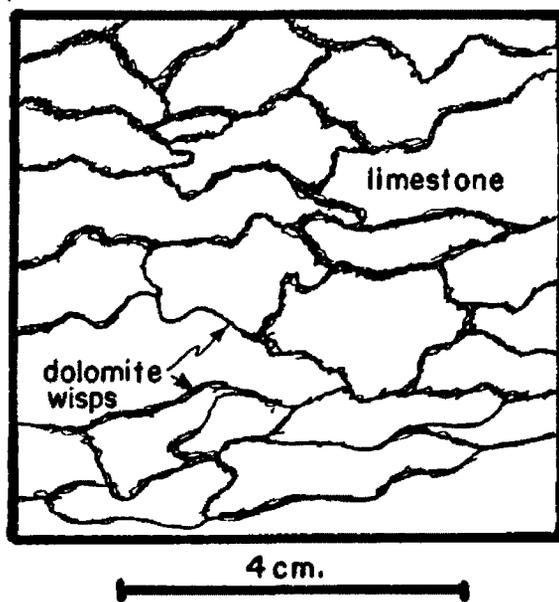


FIGURE 5

### Unit III

The upper unit, Unit III, is represented by 42.1-60 meters (137-195') section 1, 13.5-31.7 meters (44-103') section 2, 42.1-49.2 meters (137-160') section 3, 22.1-41.2 meters (72-134') section 4, and 0-17.0 meters (0-58') section 7 (Appendix I). This unit at Williams Canyon consists of massive gray limestone beds (approximately 1.5 meters thick) with common lacy solution sutures alternating with less massive brown or tan, thin bedded or lacy, dolomite beds. The alternation of limestone and dolomite beds gives this upper unit a very distinctive profile which is easily distinguished in sections 1 and 2. Chert nodules which characterize Unit II are found only at a few horizons in this unit. The uppermost 3.1 meters of this unit in sections 1 and 2 are brown and pitted by solution vugs filled with calcite.

The rocks in Unit III, sections 3,4,6 and 7 are red, pervasively dolomitized and contain abundant chert nodules. Occasional solution breccias are also present. Many of the primary depositional features and most of the structures which resulted from early post-depositional changes can be seen through the pervasive red dolomite.

Originally the sediment in Unit III was predominantly micrite and algae with some trilobite fragments, sponge spicules and bachiopod fragments. The types of algae in this unit include blue-green stromatolites, onkolites and daisy-cladacean algae. The

uppermost surfaces of individual beds within this unit are commonly sharp, planar surfaces. Intraclasts and trilobite fragments are planed off at these surfaces, indicating early subaqueous cementation followed by scour and sediment by-pass.

In all three units, detrital quartz and zircon combine to comprise up to 5 percent of the rock by point count. Original variation in iron and magnesium contents of the sediments may have ultimately resulted in alternating beds of dolomite and limestone. This point will be discussed in Episode 5 of the diagenetic sequence.

The environment of deposition of this group of rocks was probably an intertidal to subtidal marine carbonate platform. The presence of scour and by-pass surfaces indicates at times the sediment accumulated up to wave base. Intervals up to three meters thick were correlated across the area (Appendix II) indicating little topographic relief throughout the area. Therefore the area was probably tectonically stable during deposition of all three units.

## CHAPTER III

### DIAGENESIS

#### General Statement

Multiple diagenetic episodes of solution, silicification, dolomitization and calcitization appear to have occurred after deposition of the lime-mud in the following sequence: E-1 Cementation; E-2 Solution; E-3 Dolomitization; E-4 Silicification; E-5 Dolomitization; E-6 Weathering; E-7 Calcitization. These are the major episodes I can differentiate petrologically. Some of these episodes probably overlapped in time, producing variations in the above sequence. These variations are not common enough at any single locality to substantiate recognition as major diagenetic episodes and will be discussed as a group following the individual discussions of the major episodes.

#### Episode 1 - Cementation

Post-depositional subaqueous cementation and transformation of aragonite to calcite occurred rapidly after deposition of the lime sediment. Hardgrounds and flexure cracks in the lime mud which occurred at the mud-water interface are the evidence of this early cementation. Later diagenetic episodes (E-2 through E-7) all mask

the E-1 calcite cement and the abundance of the E-7 calcite makes identification of the early cement difficult. Episode E-1 occurred in all three units throughout the study area.

Early cementation of the lime-mud is evidenced by hardgrounds in all three units (Fig. 6). The hardgrounds commonly have a thin rind of red or buff iron stain on their uppermost surfaces. Cemented allochemical constituents, including intraclasts, trilobite fragments and many other types are commonly planed off at these surfaces.

The hardground surfaces are either flat, having no relief, or are irregular having a maximum relief of five cm. Both the irregular and the flat surfaces are generally planar over a lateral distance of several tens of meters and some of these surfaces can be correlated throughout the study area. Microscopically the hardgrounds are cemented by sparry calcite which is not easily distinguished from Episode 7 sparry calcite.

The cement was precipitated as either low magnesium calcite, which is indicative of the subaerial fresh water environment, or as high magnesium calcite and aragonite precipitated from sea water. I have been unable to distinguish what type of cement was originally precipitated. Transformation of metastable high magnesium calcite and aragonite to low magnesium calcite would be expected to have occurred in the 450 million years following precipitation of the cement (Bathurst, 1975). Therefore, the cement that is now calcite

Figure 6. Calcite cement (E-1) hardground overlain by a silicified (E-4) grainstone. The granoblastic quartz usually fills voids that were not previously filled with calcite. Extra-fine grained quartz partially replaced micrite intraclasts.  
(a) Daisycladacean Algae is planed off at the hardground surface. (b) Dolomite rhomb which is replaced by a single grain of quartz.



FIGURE 6a

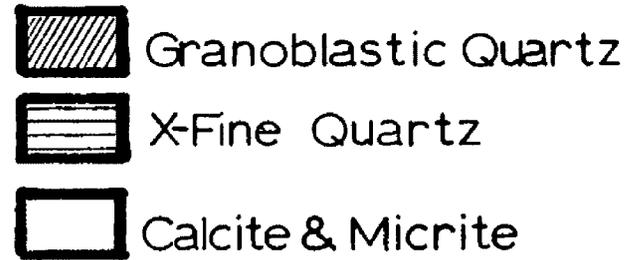
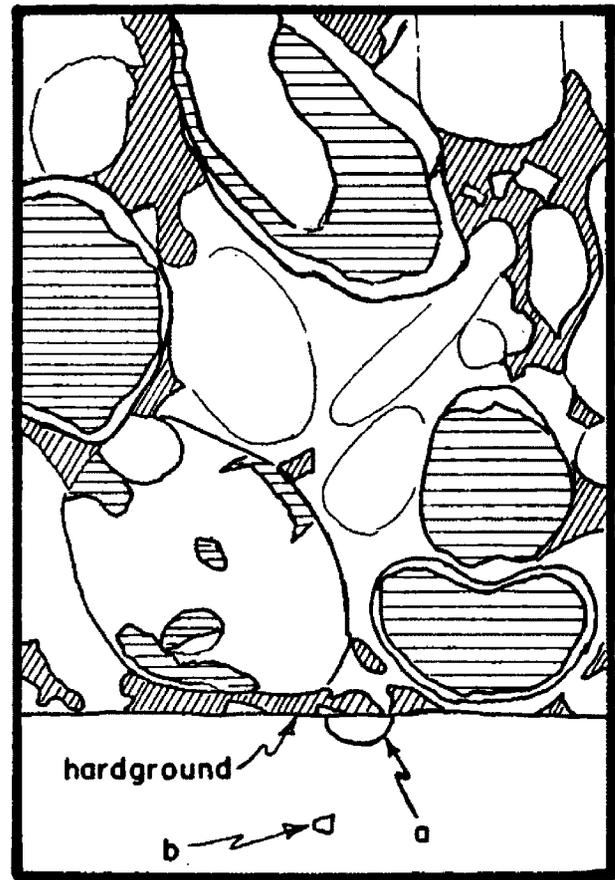


FIGURE 6b

could have been precipitated in either the subaerial environment as low magnesium calcite or in the marine environment as high magnesium calcite or aragonite.

Brittle fracture of some of the resistant limestone beds in the thin-bedded limestone during deformation at the mud-water interface indicates the lime sediment was at least partially cemented prior to its deformation (see E-2). The brittle fracture occurs as V-shaped cracks in the limestone beds formed by bending of these beds (Fig. 7). The consistency of the limestone appears to have been similar to that of stiff, but still pliable, play-dough or clay. This is indicated by the configuration of the V-shaped cracks which generally do not completely cut through the limestone beds (Fig.7). If the limestone beds were totally lithified they would have been broken into separate plates. In contrast, flexing of totally unlithified lime mud would not have formed the V-shaped cracks, but instead the sediment would have bent without breaking. The V-shaped cracks therefore indicate that the limestone beds were partially lithified by early E-1 cement prior to bending. This cement, like the cement of the hardgrounds, is not easily distinguished microscopically. However, in places where later diagenetic episodes have not obscured it, this cement is visible as sparry calcite, similar to that in the hardgrounds (Fig. 6).

Figure 7. Thin bedded limestone - Thin beds of mudstone deformed during solution leaving zones of dissolved residue between them. Edgewise intraclasts occur in the left center. (a) Broken limestone bed as a result of E-2 solution. (b) Limestone bed pinches but continues through the solution residue into the laterally adjacent bed. (c) V-shaped tension cracks created by bending the stiff mudstone bed.

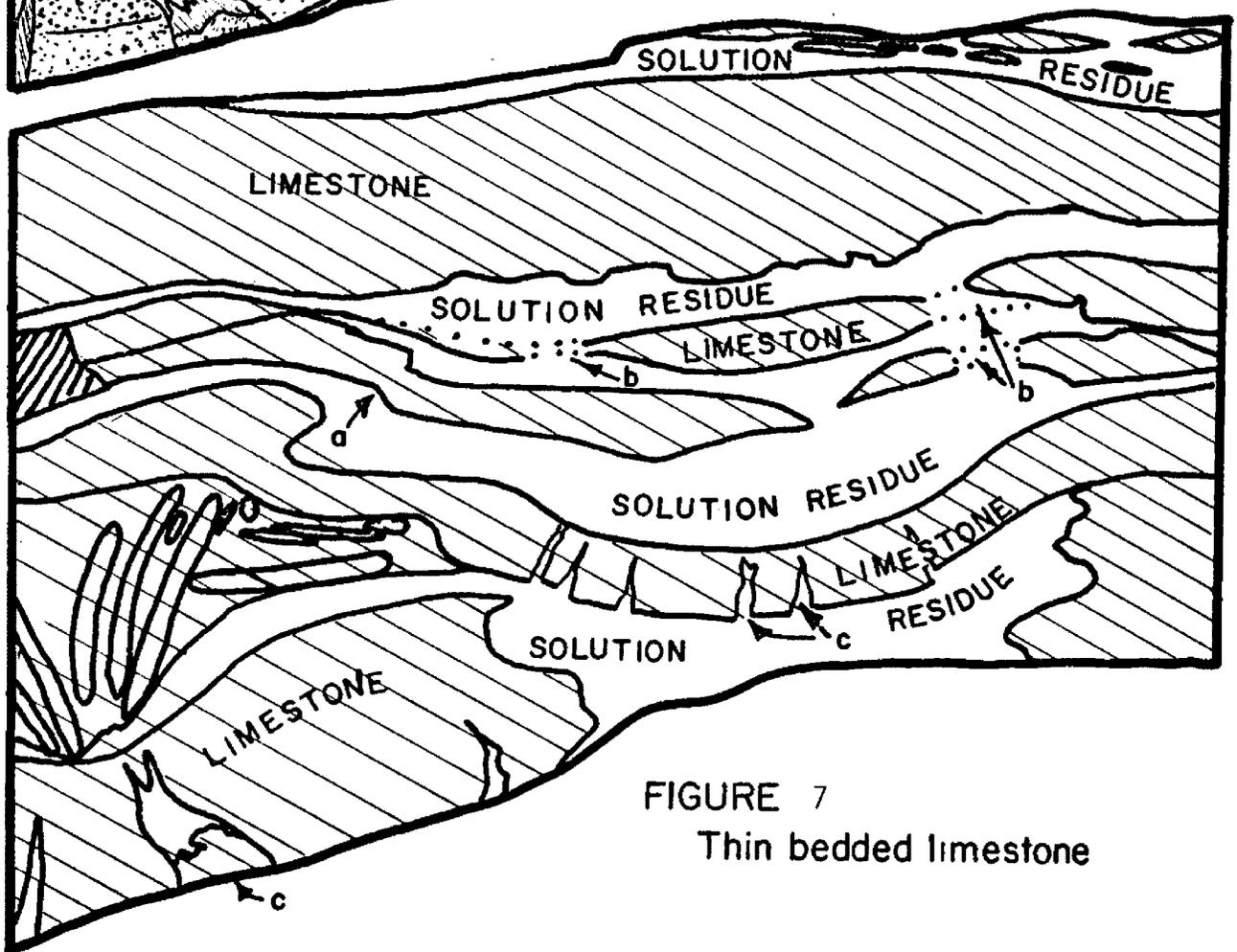
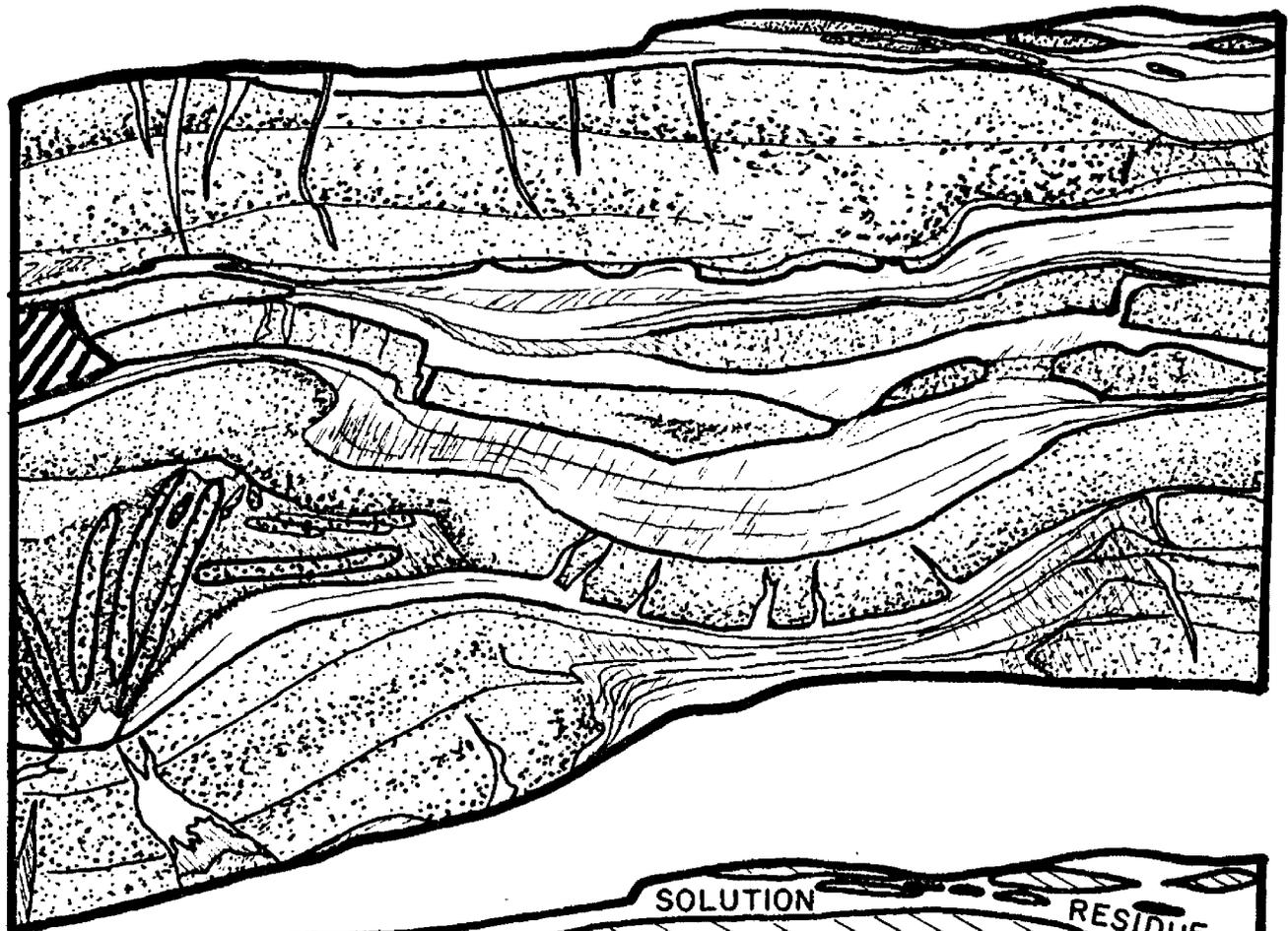


FIGURE 7  
Thin bedded limestone

Figure 8a. E-2 solution of lime mud below the mud-water interface created a pit on the sea floor resulting in slumping of the overlying mud into the pit. The micrite nodules on both sides of the pit pinch and wrap around the bottom of the pit.

Figure 8b. The pit on the seafloor was filled with an edgewise oriented intraclastic packstone. (a) V-shaped cracks indicate partial lithification prior to bending.

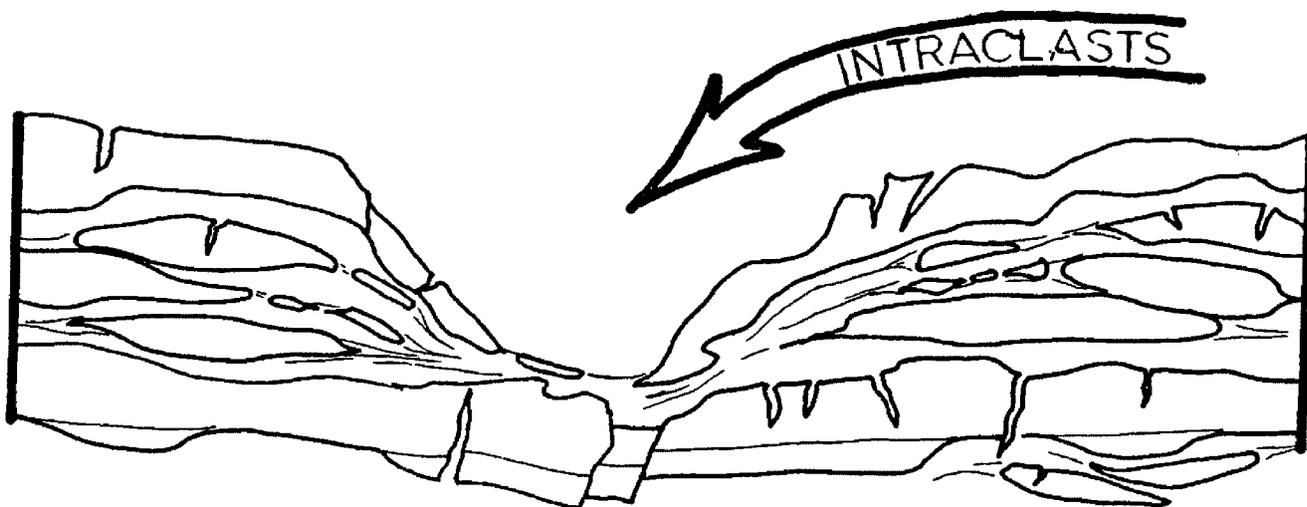


FIGURE 8a

10 cm

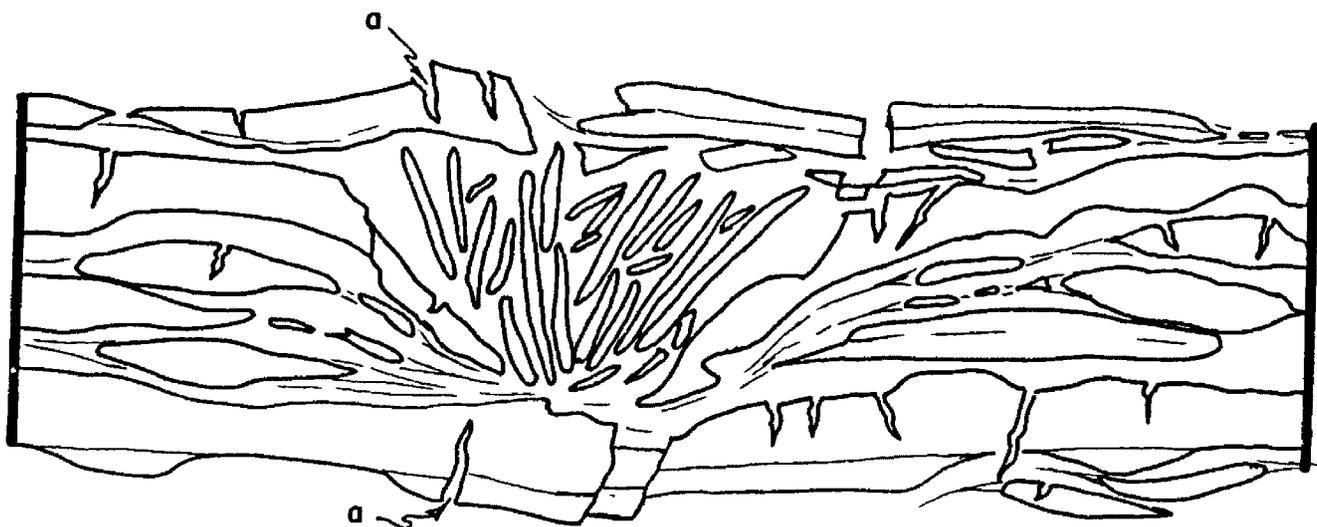


FIGURE 8b

The absence of aragonite in the rocks at both localities indicates that any aragonite in the original sediment or any aragonite precipitated as cement has recrystallized to calcite or dolomite. However, because of the complexity of the diagenesis I cannot place this recrystallization event in the diagenetic sequence.

### Episode 2 - Solution

Post-depositional solution of the lime sediment followed the E-1 cementation and resulted in two different types of limestone. One type consists of resistant weathering thin limestone beds (typically 3-8 cm thick) alternating with recessive weathering shaly appearing beds (typically 1-3 cm thick) and characterizes Unit I (Appendix I). This type is here termed thin bedded limestone (Fig. 3). The second type of limestone is here called lacy limestone, and is common in both Units II and III. It consists of a recessively weathering lacy network of solution lines dissecting massive limestone (Fig. 5). The resulting rocks is a nodular limestone in which the resistant nodules are typically 1-3 cm in height, width, and depth. In outcrop the lacy limestone commonly forms massive appearing beds whereas the thin bedded limestone forms a distinctive thinly bedded outcrop. In both types of limestone the resistant nodules or plates are generally micritic and the recessive weathering areas are the residue which remains after solution. These two types of limestones occur both at Williams Canyon and Indian Trail and can commonly be seen through the overprint of the later diagenetic episodes.

Solution of lime mud resulted in the thin-bedded type of limestone. Some resistant limestone beds are laterally continuous for ten meters, but more often they end in shaly appearing rock, resulting in bedded resistant nodules of variable length. Where the resistant limestone nodules pass into shaly appearing rock, laminae within the limestone bed become compressed. However, the laminae are continuous and can be followed from one bed or nodule, through the compressed shaly appearing rock and into the laterally adjacent limestone nodule on the other side (Fig. 7). This indicates the shaly appearing areas are composed of the nondissolved residue which remains after solution of the limestone. This form could also result from soft sediment compaction or stretching of the sediment into boudinage. However, two lines of evidence indicate the shaly appearing rock is actually the nondissolved residue which remains after solution: 1) The size and shape of the carbonate mineral grains change from equidimensional in the limestone nodules to thin plates that parallel the bedding in the shaly appearing rock due to solution from above and below the mineral grains. The density of the carbonate minerals also changes from a tightly packed mosaic in the limestone nodules to scattered elongate carbonate minerals floating in the siliceous (?) residue of the shaly appearing rock. This indicates solution reduced the size and abundance of the individual carbonate grains thereby isolating the remaining carbonate mineral grains in

the concentrated, nondissolved residue; 2) An increased concentration of non-soluble detrital quartz and zircon in the interstitial shaly appearing rock indicates the non-soluble material was concentrated by solution. The chemical or mineralogical composition of the residue has not been analyzed.

Two lines of evidence indicate the solution of lime-mud occurred at or near the mud-water interface. One is that the early solution appears to have formed small pits, up to 15 cm deep and 70 cm across on the sea floor (Figs. 7 and 8). Adjacent to the pits, limestone nodules alternate with non-dissolved residue partings. The limestone nodules all pinch out completely where they pass laterally into the pits. The laminae of the dissolved limestone nodules continue around the bottom of the pits and up the other side. This is the result of solution just below the mud-water interface because the uppermost bed slumped into the pit formed by solution of the underlying beds. These pits were filled with edgewise flat pebble conglomerates (Figs. 7 and 8). The conglomerate clearly filled a hole on the sea floor that formed by solution just below the depositional interface.

The other line of evidence of solution at or near the mud-water interface is that soft-sediment deformation just below the sediment-water interface folded the thin-bedded limestone indicating solution had occurred before the soft sediment deformation (Fig. 3). The sediments deposited over the soft sediment fold filled in the structural irregularities but were not folded.

Throughout the study area the thickness of the resistant micritic limestone beds is remarkably uniform. The beds are usually 1.5 to 5.0 cm thick. The thin limestone beds are not only uniform in thickness, they are also repeatedly interlayered with the residue which remains after solution of the limestone. This repetition suggests some cyclic or episodic process of solution. The consistent thickness of the remaining limestone beds after solution indicates the solution consistently stopped when the limestone was dissolved down to 1.5-5.0 cm thick or was dissolved to within 1.5-5.0 cm of the mud-water interface. The thickness of the recessive solution residue beds is not so uniform. However, the amount of remaining residue depends on (1) the original quantity of non-carbonate material in the rock, (2) how completely the carbonate minerals were dissolved, and (3) how much carbonate was dissolved. Assuming a reasonably continual deposition of non-carbonate material in the solution residue and in the limestone bed adjacent to it might with further study indicate how much lime mud dissolved before the beds reached that unique thickness.

Why the limestone beds are consistently thick is not now explainable. However, some of the characteristics of the solution process can be described, and these characteristics may eventually lead to such an explanation. These characteristics are:

- (1) Both the tops and bottoms of the thin limestone beds have been attacked by solution indicating that some solution certainly occurred below the mud-water interface but possibly some was at the mud-water interface.
- (2) The absence of undeformed primary structures in the solution residue indicates that the solution residue formed only below the depositional interface.
- (3) As pointed out in E-1, many of the limestone beds were stiffly cemented when the beds were bent or folded during solution (Fig. 7). Some other beds were not cemented and appear to have flowed. This probably indicates induration coincided with solution and the two may have interacted in the process.

Thus, the solution undisputably occurred immediately below the mud-water interface during or after the initial induration of the lime mud.

The second type of limestone that resulted from solution just below the mud-water interface is the lacy limestone. Increased concentrations of detrital quartz and zircon in the lacy sutures indicates this type of limestone is the result of solution. In addition bedding planes are commonly cut by the sutures. The evidence that solution occurred just below the mud-water interface is that lacy sutures are cut by scour surfaces (Fig. 9). The solution sutures formed before scour but at a depth shallow enough

Figure 9. Lacy limestone that was created by E-2 solution of limestone is cut by a scour surface indicating the solution occurred just below the mud-water interface. This was followed by deposition of the overlying fossiliferous grainstone.

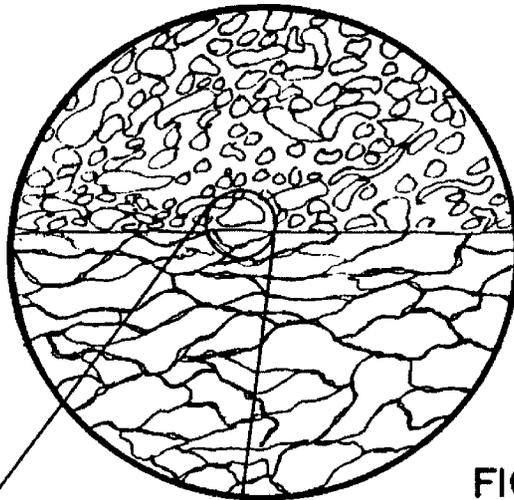


FIGURE 9a

4 cm

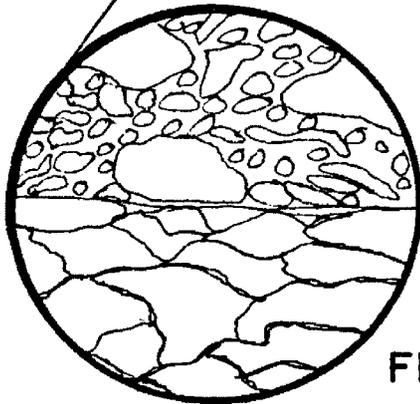


FIGURE 9b

2 cm

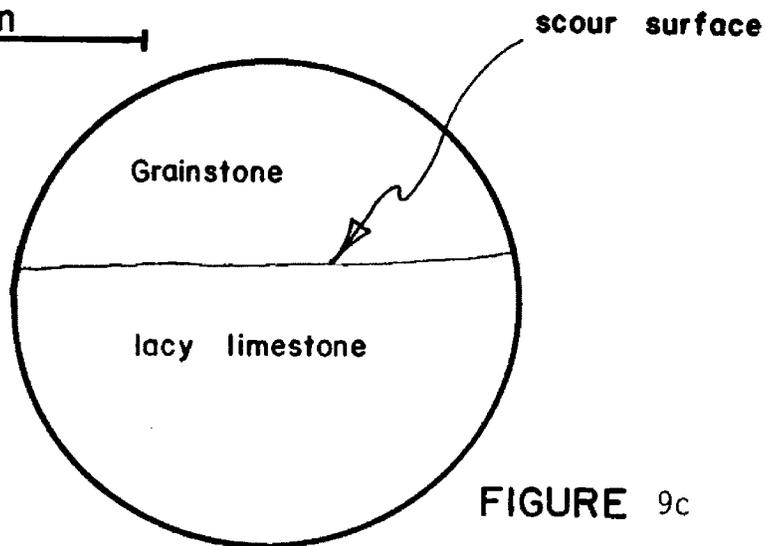


FIGURE 9c

to be cut by the scour. Later stages of early diagenetic mineralization crosscut the sutures supporting the early diagenetic interpretation. The lacy sutured limestone occurs throughout all three units but is most common in Units II and III (Appendix I).

#### Episode 3 - Dolomitization

Several stages of post-depositional dolomitization occurred in the Manitou Formation. This first episode of dolomitization was minor in comparison to the two later episodes and resulted in clear, generally euhedral to sub-euhedral rhombs .2 mm in size (Fig. 10). Both the micrite and the allochems were dolomitized, but dolomitization was minor and resulted in only sparse dolomite rhombs. The first dolomitization did not appear to obliterate any of the primary sedimentary structures in the sediment.

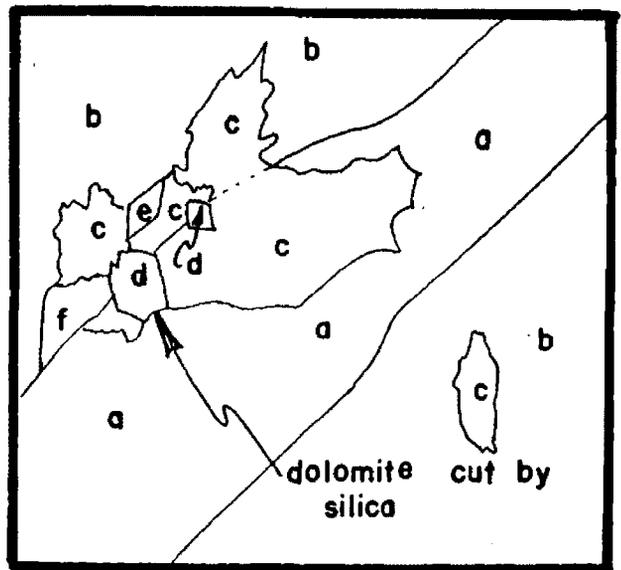
The evidence for this dolomitization occurring as the third episode of the diagenetic sequence is that the dolomite has replaced both fossil fragments and the E-2 solution residue areas. Conversely some dolomite rhombs have been replaced by quartz (Fig. 10), the fourth diagenetic episode.

#### Episode 4 - Silicification

The first period of silicification is found in all three units throughout the study area. It characterizes Unit II where it forms abundant white chert nodules which parallel bedding. Coarse to very fine granoblastic quartz from this episode of silicification replaced

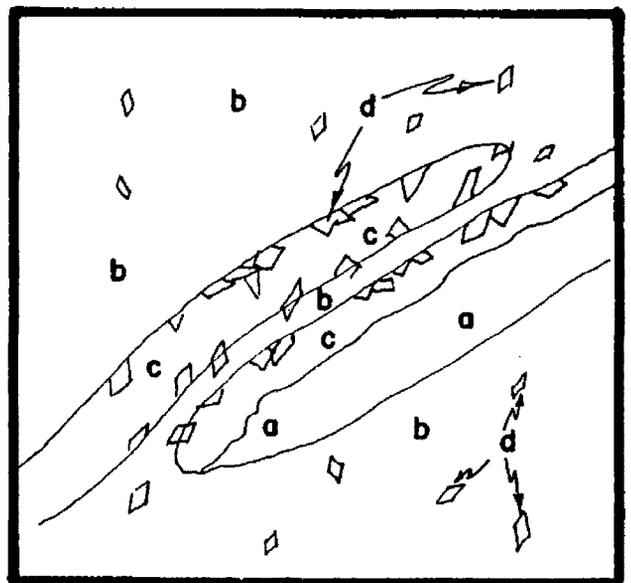
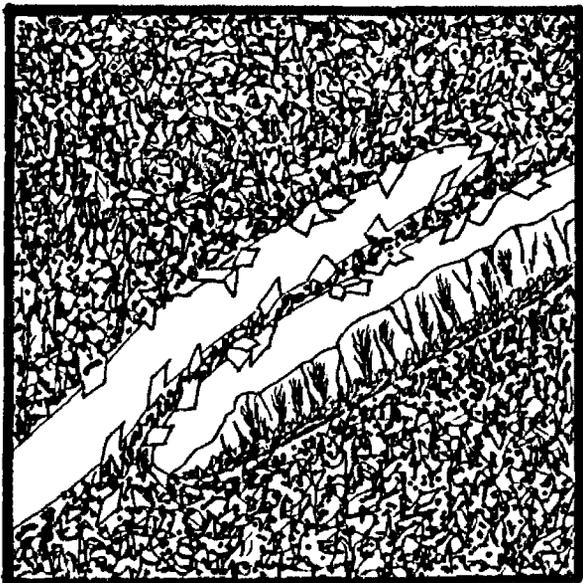
Figure 10. Silicified trilobite fragment in micrite. Calcite trilobite fragment (c) in micrite (b) is partially dolomitized (E-3) (d). E-4 silicification resulted in chalcedony replacing most of the trilobite fragment (a), granoblastic quartz replacing some of the micrite (f) and a single crystal of quartz (e) replacing a dolomite rhomb. Note the E-3 dolomite rhomb is cut by the E-4 chalcedony. This is rarely found. The common relationship is shown in Fig. where the silica and the dolomite do not meet.

Figure 11. Partially dolomitized and silicified trilobite fragments in micrite. Calcite trilobite fragments (c) in micrite (b) are partially replaced by E-4 chalcedony (a). E-5 dolomite (d) replaced both the micrite and the calcite. Many of the dolomite rhombs truncate the calcite-micrite boundary. Note the sharp edge of the chalcedony-micrite boundary. If dolomitization had preceded the E-4 silicification this sharp boundary would have been lost as in Fig. 10. The sharp chalcedony-micrite boundary indicates the dolomitization is post silicification and therefore E-5 dolomite.



1.5 mm

FIGURE 10



6.0 mm

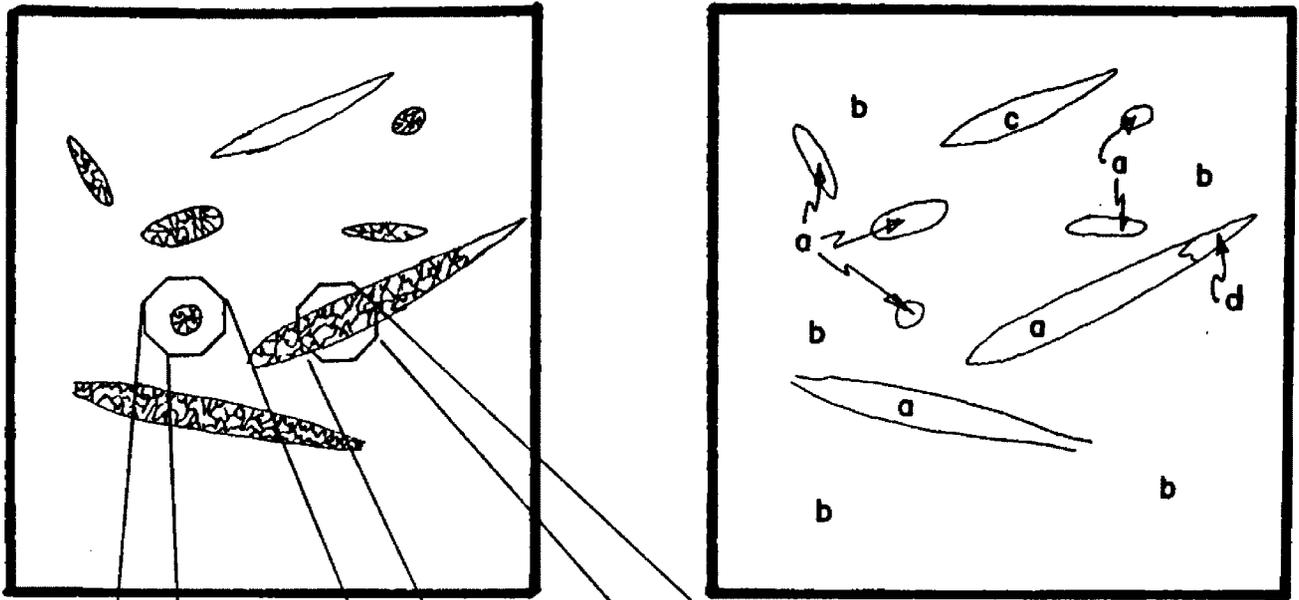
FIGURE 11

allochemical grains, E-1 cement, E-2 solution residues, E-3 dolomite and fills many of the voids in the rocks. A very fine grained nearly isotropic chert commonly replaced micrite. Occasionally chalcedonic quartz lines voids and wraps around silicified allochems. Dolomite rhombs from the E-5 dolomitization commonly replace the finer grained E-4 cherts thereby bracketing this episode of silicification between the E-3 and E-5 dolomitization events. The habit of the chert takes on the habit of the carbonate it has replaced, although the two habits are not identical. For instance, silicification of trilobite fragments which are fibrous calcite crystals oriented perpendicular to the carapace surface resulted in chalcedonic quartz with a similarly oriented fibrous habit. Silicification of calcareous sponge spicules results in granoblastic quartz which is coarser in the center and radiates outward to finer nearly isotropic chert at the edges giving the spicules a pseudo-radial habit (Fig. 12). Micrite is commonly replaced by very fine grained, nearly isotropic chert. These are a few examples of the preservation of the primary sediment by this silicification.

This episode of silicification also replaced some dolomite. This replacement was unique since single dolomite crystals are replaced by single quartz crystals (Fig. 10). These quartz grains are easily confused with the detrital quartz silt in the rock, however, the distinct rhombohedral shape and uniform size distinguishes them.

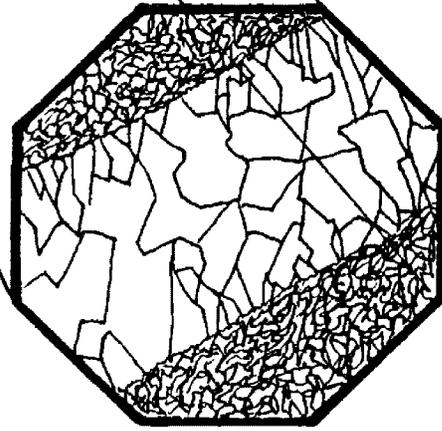
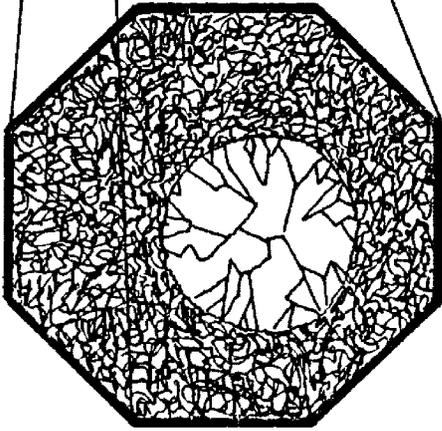
Figure 12a. Silicified sponge spicules in micrite. Calcite sponge spicules (c) in micrite (b) are partially replaced by silica (a) leaving remnants of the original calcite spicules (d). Note the selective silicification of the spicules leaving the micrite unsilicified.

Figure 12b. Note the pseudo-radial quartz growth resulting from the crystal size increasing into the void. This indicates the calcite was progressively dissolved during silica precipitation.



1.0mm

FIGURE 12a



0.05mm

FIGURE 12b

Micrite intraclasts are commonly replaced or partially replaced by silica. The presence of micrite coatings around some silicified intraclasts possibly suggests the intraclasts were silicified prior to being ripped up and accreted. However, the size and roundness of the chert intraclasts is similar to that of the micrite intraclasts in the same rock, suggesting later selective silicification of the intraclasts. Commonly the silica has selectively replaced micrite but did not replace calcareous sponge spicules in the micrite. This indicates the process of replacement was selective and the micrite rind around the intraclast may have been composed of slightly more stable carbonate minerals than the interior of the intraclast, with respect to the silicifying solution. Rarely the fine grained chert in the intraclasts grades into the coarser grained granoblastic quartz between the intraclasts. This probably indicates the silica replaced the intraclast and then continued to fill the adjacent void without a break. Nowhere did I find a distinct contact between chert intraclasts and void filling granoblastic quartz which could indicate two silicification episodes. Thus the silicification replaced intraclasts and filled voids thereby indicating it occurred at any depth below the mud-water interface.

This silicification formed elongate chert nodules which parallel the bedding. Some horizons of concentrated bedded chert nodules can be correlated throughout the study area (E.G. 6.1-9.2 meters thick horizon of dense nodular chert beds at 24 meters section 1, 23.7

meters section 3, and 1 meter section 4, Appendix II). Since the chert nodules parallel bedding everywhere and are laterally continuous throughout the study area, I believe the silicification was contemporaneous with deposition. However, the nodules are clearly of replacement origin and not a primary silica precipitate. Therefore, I believe the silicification of each nodular interval occurred at a shallow depth below the mud-water interface and continued as deposition took place.

This silicification may be explained by the decay of organic material increasing the partial pressure of  $\text{CO}_2$ . This could locally lower the pH of the sediment pore fluids thereby precipitating dissolved silica (Fig. 14). The abundance of silicified fossil fragments, particularly sponge spicules, supports the association of the silicification and the organic material. The pore fluid surrounding the carbonate grains would be expected to maintain its original pH of 8.0-8.3 (Krauskopf, 1967). A decreased pH to less than 7.3 would dissolve calcium carbonate on one hand and on the other, where concentrations of dissolved silica exceed 120 ppm, amorphous silica would precipitate (Fig. 14 from Middleton et al, 1972). A concentration gradient between the site of organic decay and the carbonate sediment would result. Dissolved carbonate would migrate away from the decaying material and dissolved silica in the carbonate sediment would migrate towards the decomposition. This process would continue until the organic decay ceased (see Seiver, 1962).

Figure 13. Eh-pH diagram for iron from Middleton et al., 1972.

Figure 14. Solubility curves for calcite, amorphous silica and quartz. Both silica and calcite can be expected to precipitate at common surface conditions with a pH between 7 and 8.5

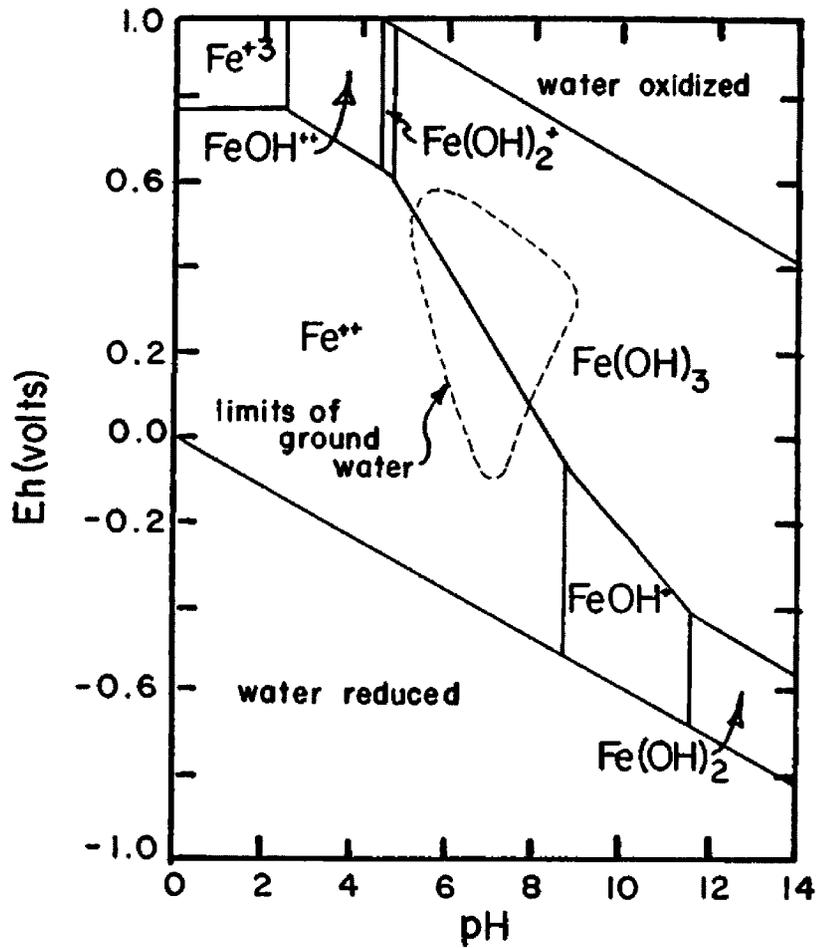


FIGURE 13 - from Middleton et al., 1972

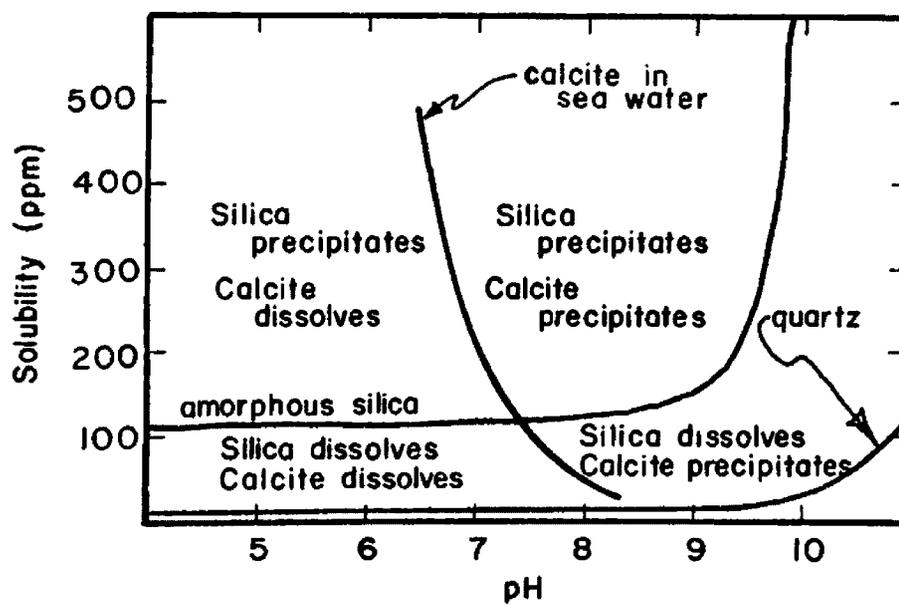


FIGURE 14  
from Middleton et al., 1972

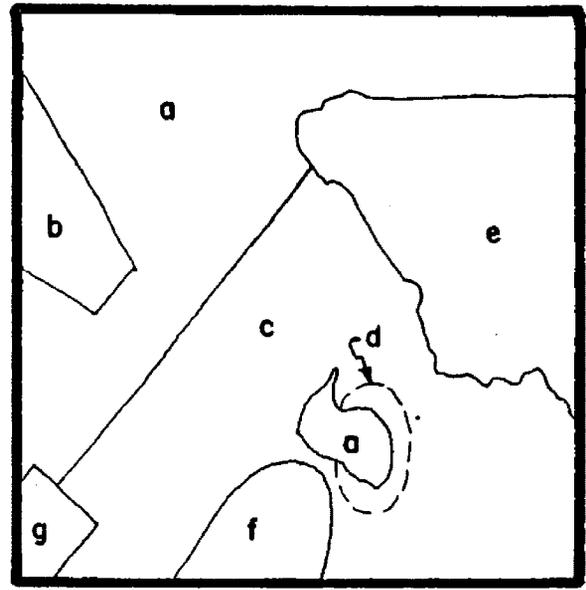
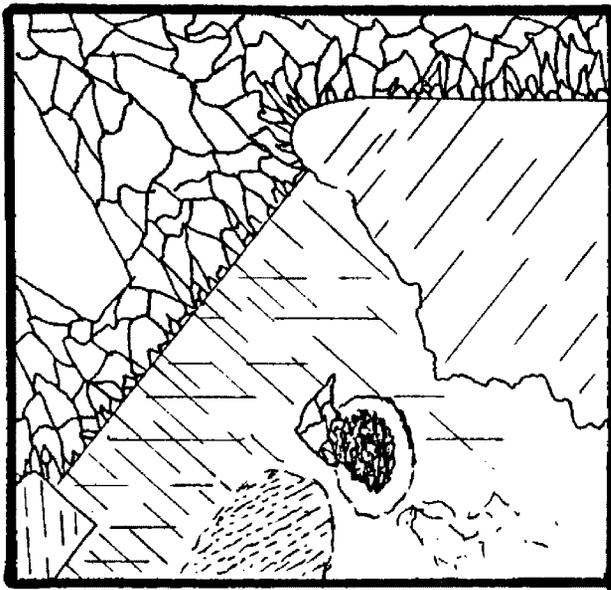
Bedded chert nodules may be the result of bedded organic concentrations.

#### Episode 5 - Dolomitization

An episode of post-silicification, dolomitization took place at both Indian Trail and Williams Canyon Localities. This dolomitization is most common in Unit III but it also occurs in Units I and II (Appendix I), where preferential dolomitization of certain beds resulted in alternating beds of limestone and dolomite which can be easily correlated through out the study area (Unit III correlations, Appendix II). Microscopically this dolomite commonly replaced the chert formed during Episode 4 as evidenced by euhedral dolomite rhombs, with sharp unetched crystal faces, floating in the fine-grained chert (Fig. 16). It could be argued that the silicification selectively replaced the limestone and did not replace the dolomite. If this were the case, I would expect to find the dolomite rhombs to be embayed by the chert, but the crystal faces of the dolomite are sharp, unetched surfaces, indicating the dolomite formed after the chert. As even more convincing line of evidence for a major episode of dolomitization following the silicification is that fine textures in the original carbonate sediments were preserved by E-4 silicification but obliterated by E-5 dolomitization. E-4 silicification effectively preserved the primary constituents and those that were not silicified were dolomitized by E-5 dolomitization and forever destroyed.

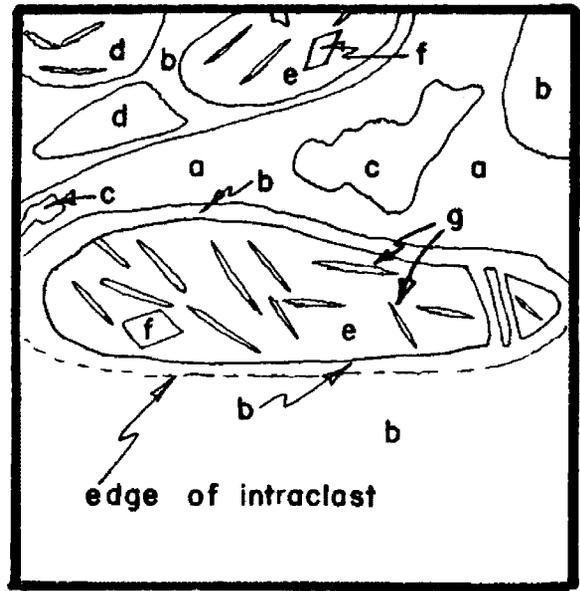
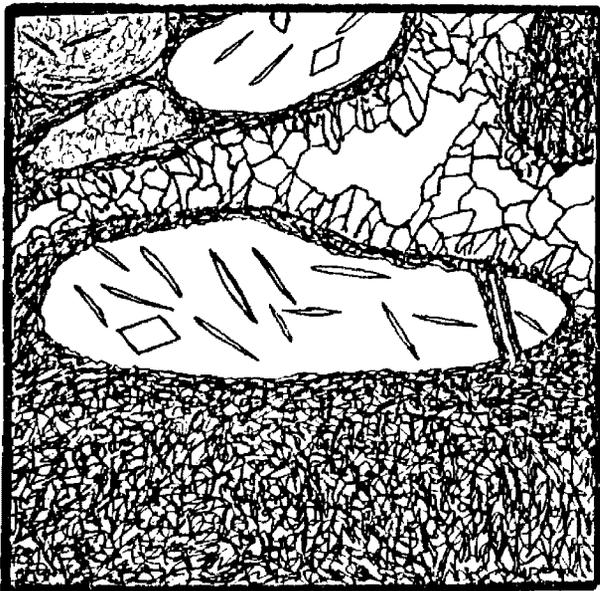
Figure 15. Echinoderm fragment (f) with E-1 calcite overgrowth (c) that partially replaced the intraclast (d). E-1 calcite cements (c,e,g) have E-4 silica (a) precipitating on the surface of calcite crystals. E-4 silica (a) partially replaced the intraclast (d) and some E-1 calcite. Note the calcite crystal (b) that does not have the E-4 silica growing on it. This is probably the late E-7 calcite.

Figure 16. Intraclasts (d,e) in micrite (b) are silicified (E-4) with either medium grained quartz (d) or extra fine grained, nearly isotropic quartz (e) leaving calcareous sponge spicules (g) unsilicified. The extra fine grained silica (e) is actually black under x-nicols but for reproduction purposes it is left white. E-1 calcite cement (c) that at one time filled a void space is partially replaced by E-4 silica (a) that precipitated on the micrite (b) and gets coarser inward. E-5 dolomite (f) floating in the fine grained chert. Walker (1964) cites this as evidence for dolomite replacing silica.



1.5 mm

FIGURE 15



2.0mm.

FIGURE 16

Where the limestone beds are interstratified with dolomite beds the dolomite beds contain E-4 chert nodules preserving the fabric of the original limestone. Thus the dolomite replacement of limestone was exceedingly selective leaving sharp boundaries between the dolomite beds and the limestone beds. The fact that individual dolomite beds can be correlated throughout the area indicates the dolomite was in part strataform.

The dolomitization appears to have followed the more permeable zones in the rock. This is evidenced by dolomitization of (1) the lacy solution wisps in the lacy limestone; (2) the residues in the thin bedded limestone; (3) worm (?) burrows; and (4) zones of obvious increased permeability. Beds that were well cemented (E-1) prior to E-5 dolomitization were not dolomitized during E-5 since the cement sufficiently reduced the porosity of those beds. Therefore, I believe the preferential dolomitization of individual beds followed primary porosity and was limited by the E-1 early cement.

#### Episode 6 - Weathering

Weathering occurred during the post-Manitou pre-Devonian hiatus and resulted in extensive solution, dolomitization and silicification only at the Indian Trail Locality (Fig. 2). There the rocks are red or dark brown and are pervasively dolomitized in the upper two-thirds of the section. Solution breccias in the uppermost part of the section at Indian Trail (30.7-41.2 meters, section 4) probably

fill sink-holes. Above the Manitou Formation at this locality is a massive quartz siltstone bed of unknown age which is up to eight meters thick. This is overlain by the Devonian Williams Canyon Limestone. The chert nodules at the Indian Trail Locality are larger and more abundant than those at Williams Canyon. By contrast the carbonate rocks at Williams Canyon are gray or buff in color and only the upper 3.2 meters of the section have a brown weathering, vuggy dolomite which is red on a freshly broken surface and resembles the weathered carbonate rocks at the Indian Trail Locality. The vugs are solution vugs filled with calcite. The uppermost surface of the Manitou Formation at Williams Canyon is an irregular surface but other than the small vugs it does not have the solution features that characterize its counterpart at Indian Trail. These differences in the diagenesis of the two localities followed the E-5 dolomitization that occurred in a similar way at both localities.

E-6 weathering included three diagenetic processes; dolomitization, silicification and solution that are considered sub-episodes 6a dolomitization, 6b silicification and 6c solution. These three processes appear to overlap somewhat in time since they are all limited to the Indian Trail Locality and they are all difficult to separate petrologically. These processes are therefore grouped into a single episode, E-6 weathering, but the processes are discussed separately. Following those discussions I will demonstrate how

weathering caused the simultaneous occurrence of all three processes.

Episode 6a- Dolomitization. The rocks at the Indian Trail Locality are pervasively dolomitized except the basal 8.6 meters which is similar to the rocks in Unit I at Williams Canyon. This dolomitization obliterated most of the primary structures in the rocks. In outcrop some of the primary structures visible in the carbonate rocks are the algal stromatolites which are only faintly discernable on weathered surfaces. Also distinguishable through the pervasive dolomitization are many of the previous diagenetic changes. The most easily distinguished are the lacy and thin bedded limestones resulting from E-2, the chert nodules from E-4 and the porosity controlled dolomitization from E-5. Since the previously discussed diagenetic episodes can be seen through this dolomitization but are altered by it, this pervasive dolomitization occurred after the previously discussed episodes.

Microscopically this dolomite consists of anhedral dolomite crystals with occasional subhedral to euhedral rhombic crystals which are commonly zoned with ferric iron bands. The crystal size ranges up to 0.5 mm. In thin section this dolomitization has obliterated all evidence of the previous diagenetic episodes except the E-4 silicification. Because later E-6b silicification may be confused with

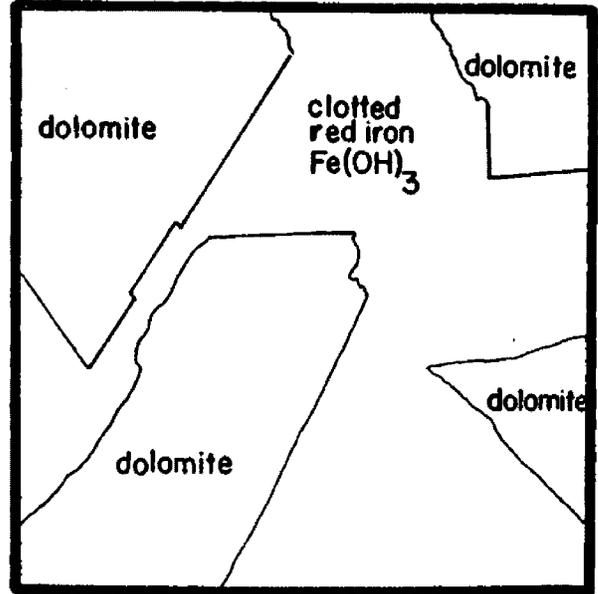
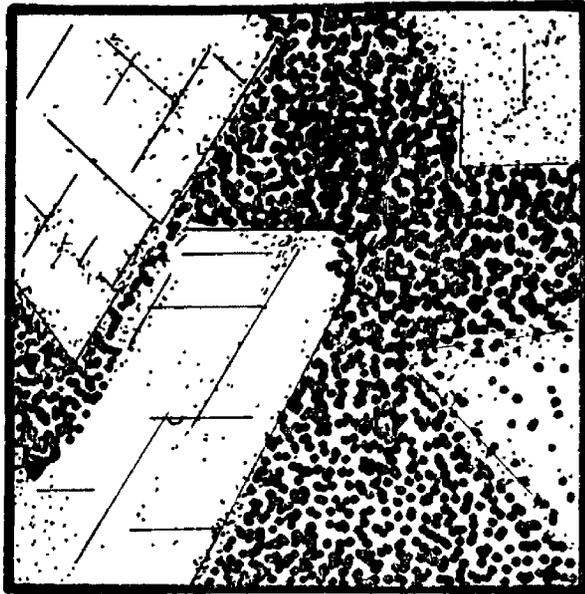
E-4 silicification and this E-6a dolomite may be confused in places with E-3 and E-5 dolomites conclusive evidence that will pin down the time relationship of this dolomitization to the other diagenetic processes of E-6 is not possible. Occasional silicified dolomite rhombs may indicate that this dolomitization preceeded the 6b silicification. However, these are rare and the silicified dolomite rhombs could be the result of earlier episodes.

Associated with this dolomitization is a pervasive red stain of oxidized iron that was either freed from an ankeritic dolomite lattice or was precipitated from interstitial solutions. Zoned dolomite rhombs demonstrate that some iron was incorporated in the original dolomite lattice but most of the dolomite is not zoned. Most commonly the red stain coats the dolomite and fills pore spaces with blotches of ferric iron (Fig. 17). The coatings are probably due to ferrous iron in solution in slightly acidic water precipitating out as ferric iron when the solution becomes more alkaline in contact with the dolomite (Fig. 13).

Swett (1964) determined by colorometric titration with  $\text{KMnO}_4$  that the red dolomites in the southern exposures of the Manitou Formation contained an average of .53 percent iron whereas the buff colored dolomites at Williams Canyon contained an average of only .29 percent iron. He concluded that the original carbonate had a high iron content that led to selective dolomitization of the iron

Figure 17. Clotted red iron  $\text{Fe}(\text{OH})_3$  on surfaces and interstitial to E-6a dolomite rhombs.

Figure 18. Silica-dolomite boundary. (a) Granoblastic quartz; (d) Dolomite; (g) Single crystal of quartz replacing dolomite. Note the vague quartz-dolomite boundary.



0.05mm

FIGURE 17



0.1mm

FIGURE 18

rich limestones producing ankeritic dolomite. The association of red iron stain and E-6a dolomite is also obvious at Indian Trail and as I shall discuss (page 59, text) both probably formed by fresh ground water, with dissolved iron, mixing with sea water.

Silicification - E-6b. The Indian Trail outcrops are much more silicified than those of Williams Canyon. At Indian Trail the chert nodules are considerably larger and more abundant than at Williams Canyon. In many places the silicification is so complete it forms white and occasional red chert beds. This increased silicification at Indian Trail is a separate episode from the E-4 silicification which occurred at both localities.

Most but not all of the larger chert beds and nodules are composite nodules consisting of inner modules of E-4 chert and outer rims of the E-6b silica (Fig. 19). In these composite nodules the E-4 nodule served as a nucleation site for the later E-6b silicification. The composition of inner nodules, described in detail in E-4, can be summarized as granoblastic quartz replacing allochemical constituents including fossil fragments, peloids, intraclasts and sponge spicules. Some chalcedony and drusy quartz fills voids between the silicified allochems but granoblastic quartz does not replace dolomite rhombs.

Many of the outer rims on the larger nodules of the E-6b silicification have granoblastic quartz replacing dolomite rhombs and

Figure 19. Composite nodules from Indian Trail.  
The inner nodule is clear white E-4 chert  
whereas the outer E-6b chert nodule has  
abundant pores which are the result of  
solution of the E-5 or E-6a dolomite that  
was not replaced by silica.

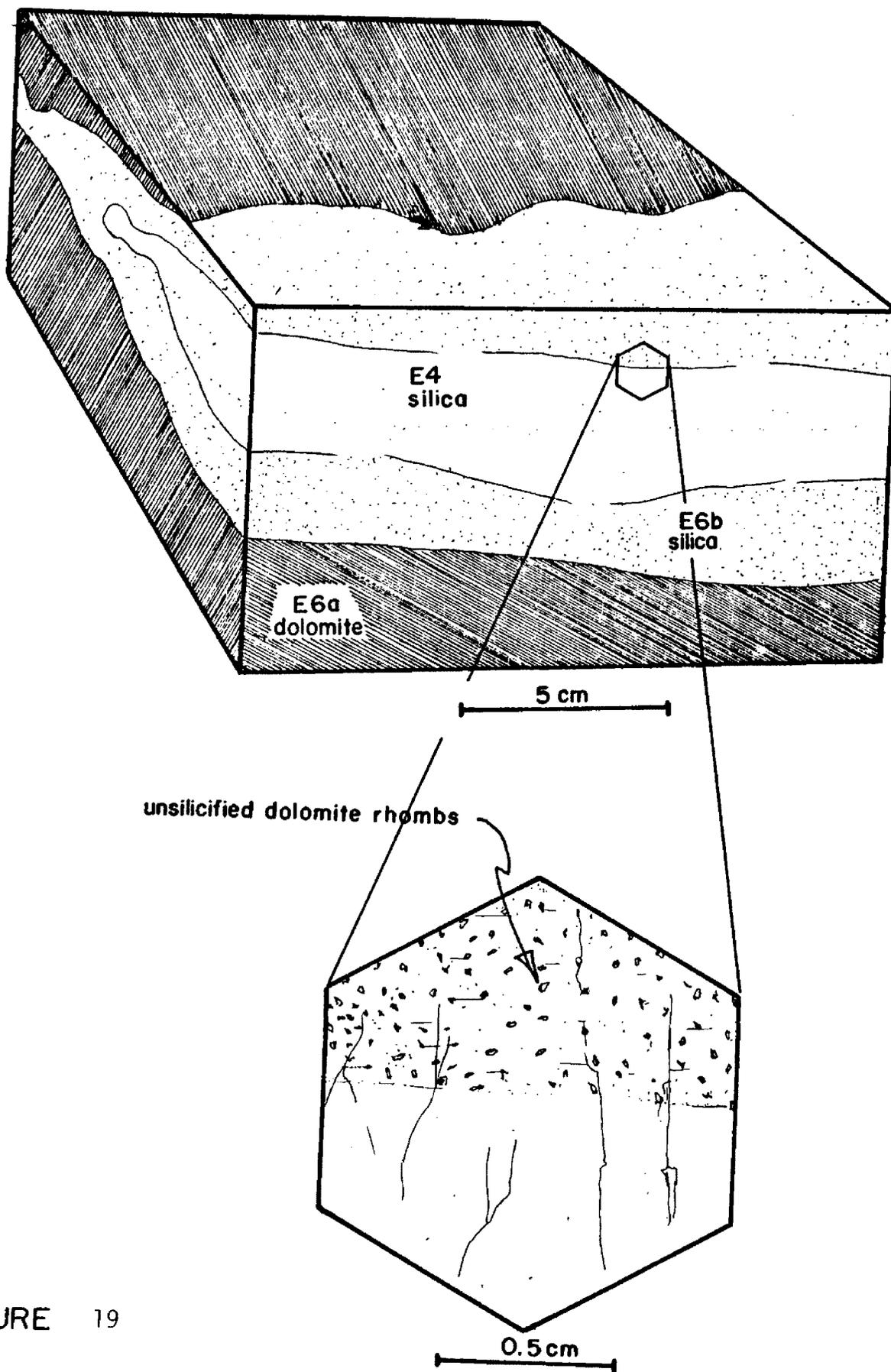
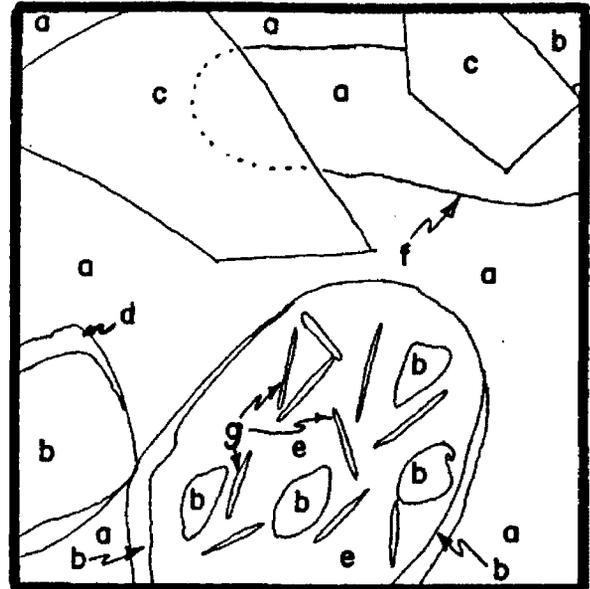
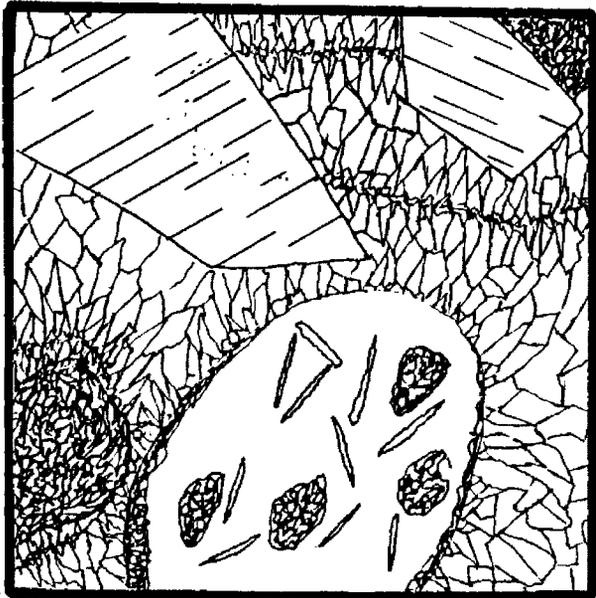


FIGURE 19

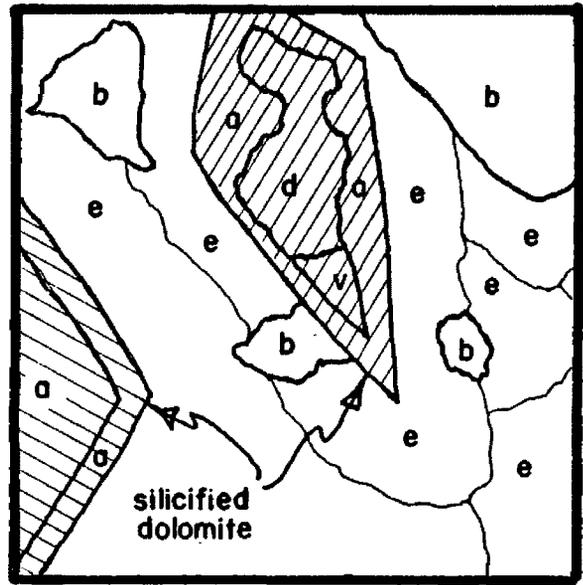
Figure 20. Micrite intraclasts with calcareous sponge spicules (g) are replaced by E-4 granoblastic quartz (a) and extra fine grained chert(e). The extra fine grained chert is black under x-nicols but is left white for reproduction purposes. Silicification totally replaced an intraclast (f) leaving only a silica rind as a ghost of the original intraclast. A silica rind (d) resulting from partial silicification of an intraclast. E-7 calcite (c) replaces E-4 silica and clearly truncates the silicified intraclast (f).

Figure 21. Silicified dolomite rhombs. E-5 or E-6a dolomite rhomb (d) replaced by E-6b granoblastic quartz (a). E-6b chalcedony precipitated on the granoblastic quartz (a). (b) Fine grained silica replacing micrite; (v) void space.



1.5 mm

FIGURE 20



0.4 mm

FIGURE 21

rhombic holes left by dissolving out those dolomite rhombs that were not silicified (Fig. 21). Allochems which were not preserved by the first E-4 silicification were commonly obliterated by the E-5 and E-6a dolomitizations before E-6b silicification. The E-6b silicification resulted mostly in chalcedony precipitating on the E-4 silica which is mostly granoblastic quartz. However some granoblastic quartz can be identified as E-6b silica, occasionally causing problems in identification. The compositionally different E-6a chalcedonic rims on the granoblastic quartz E-4 nodules indicates that two separate silicification episodes, a pre-dolomite and a post-dolomite, occurred at Indian Trail.

The E-6a silica cannot everywhere be differentiated from E-4 silica because of the similar compositions of the two episodes and the complex overall diagenesis. Chalcedony and granoblastic quartz were precipitated during both the E-4 and E-6b silicifications making positive identification impossible. Generally the granoblastic quartz resulted from E-4 and chalcedony resulted from E-6b.

The time relationship of the E-6a dolomitization to the E-6b silicification is not obvious. Most often the chert dolomite boundary is indistinct (Fig. 18). Because occasional dolomite rhombs are silicified and nowhere is E-6b silica replaced by dolomite, E-6a, dolomite probably preceded E-6b silicification.

Solution - E-6c. Occasional sink holes and carbonate breccias in the upper portion of the Manitou at Indian Trail indicates a period of post-Manitou, pre-Devonian solution. The beds overlying the sink holes are collapsed down into the sink holes. These solution features are found mostly in the upper 10 meters of section 4 (Appendix I ). The breccias do not extend far enough down into the Manitou to expose the relationship of the chert nodules to the solution breccias.

In E-6a dolomitization (page 48, text) the association of the E-6a dolomite to red iron oxide stain was attributed to iron precipitating from slightly acidic solutions. This E-6a solution is the result of slightly acidic water dissolving the carbonate minerals and carrying dissolved iron. Precipitation of the iron would take place because the acidic pore water will equilibrate with the surrounding carbonate by dissolving carbonate minerals, thereby increasing pH and precipitating iron (Fig. 13).

Both the Williams Canyon and Indian Trail sections are about 61 meters (196') thick. Therefore this solution did not significantly thin the Indian Trail section but merely weathered the outcrop to a distinctive red terra rossa color. Overlying the Manitou Formation at this locality is a white quartz siltstone of unknown age up to fifteen meters thick and this is overlain by the gray Devonian Williams Canyon Limestone. Thus the red terra rossa in the Manitou Formation

at Indian Trail post-dates the deposition of the Manitou but pre-dates deposition of the overlying Devonian Williams Canyon Limestone.

Discussion - Episode 6. It is apparent from the association of the three processes of E-6 that they are all in some way related to post-Manitou weathering. To propose that three geochemically different processes, solution of carbonate minerals, dolomitization and silicification are all related to a single geological process seems rather outrageous. However, a geochemical model similar to the Dorag model for dolomitization (Badiozamani, 1973) can account for the "outrageous" proposal. Badiozamani (1973) devised a model for dolomitization that involves the mixing of phreatic fresh water with phreatic sea water in the pore spaces of carbonate rocks (the *mischungskorrosion* effect). In the phreatic zone, which is simply below the water table, a fresh water-seawater boundary exists where ions in sea water can be easily exchanged with fresh water ions. The solubility curve for calcite is a non-linear function and the mixing of two different waters saturated with respect to calcite creates a third water undersaturated with respect to calcite (Fig. 22) (Runnels, 1969). Badiozamani (1973) demonstrated that the solubility curve for dolomite is not like calcite and that mixing 5-30 percent sea water with fresh water produces a water supersaturated with respect to dolomite and undersaturated with respect to calcite (Fig. 24). Under these conditions calcite will be dolomitized with

Figure 22. Calcite solubility, with respect to partial pressure of  $\text{CO}_2$ . Mischungkorrosion effect is where undersaturation results from the mixing of two waters saturated with respect to calcite. From Runnels, 1969.

Figure 23. Solubility of amorphous silica with respect to pH. Note the Mischungkorrosion effect results in supersaturation of a mixed water. Solubility curve from Middleton et al., 1972.

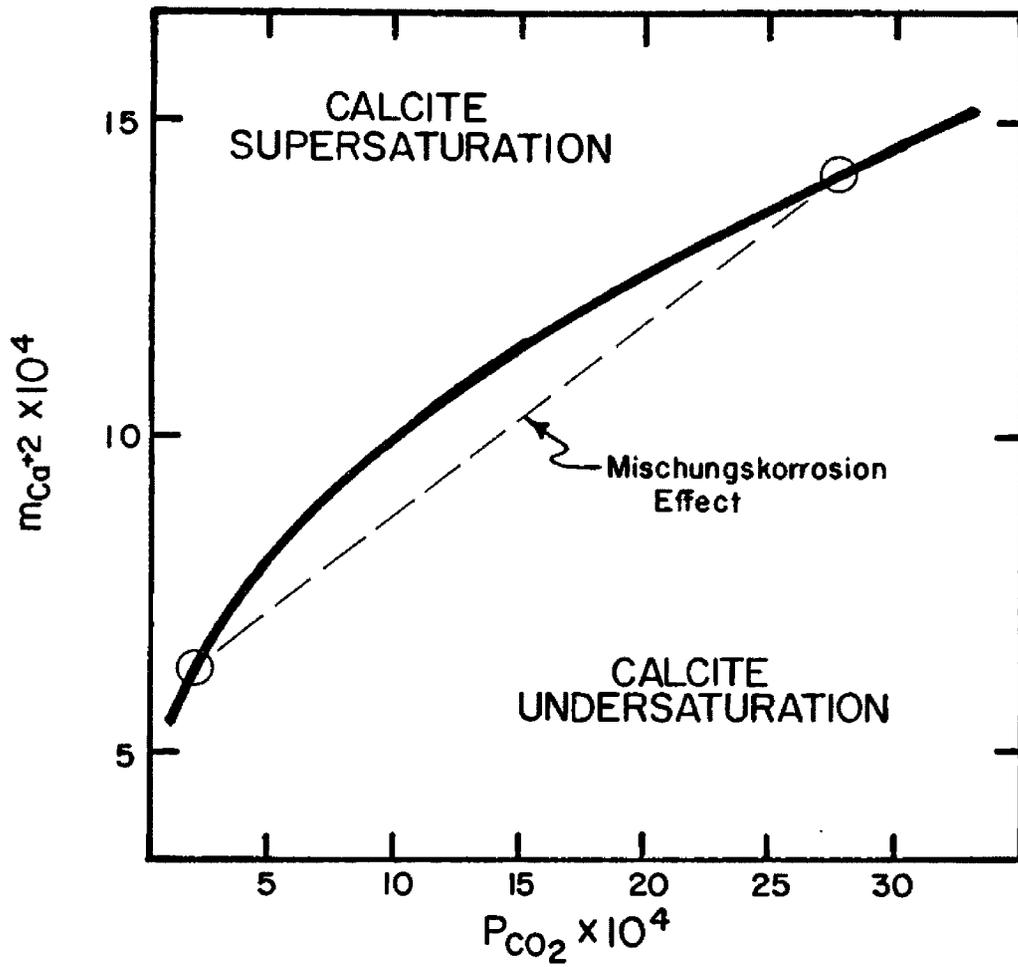


FIGURE 22

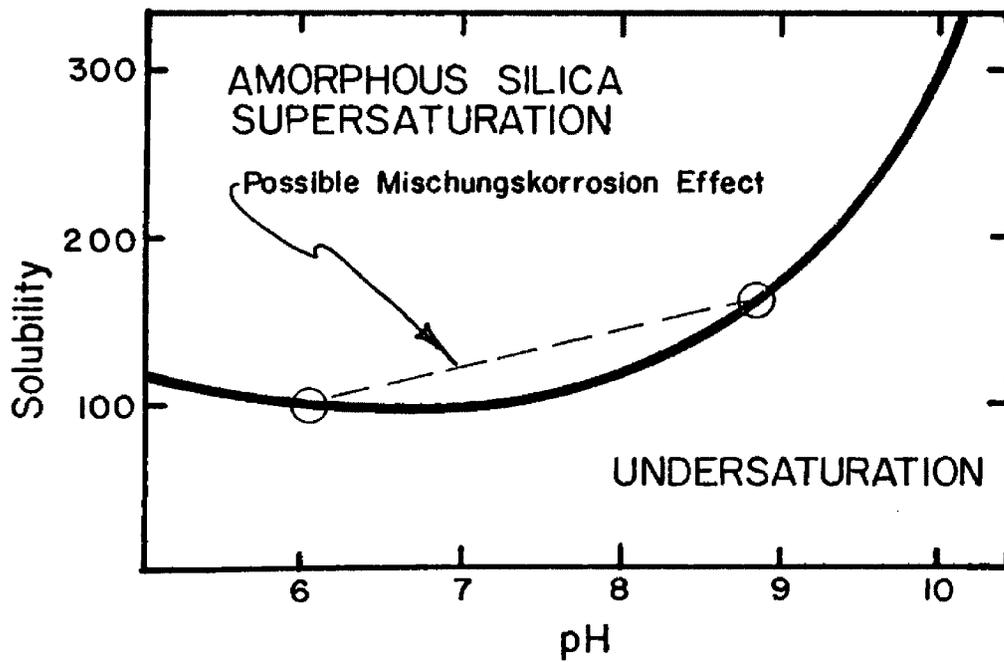


FIGURE 23

a Mg/Ca ratio of 1:1 or more, well below the Mg/Ca ratio of normal sea water (Krauskopf, 1967).

In order to complete dolomitization a large quantity of fresh water must continually mix with sea water in the rocks to keep the saline concentration between 5 and 30 percent normal sea water (Fig. 24). The large land surface generally collects enough water to keep the process operational with enough hydrostatic head to pump the fresh water into the sea water.

The basic principle of the drag model for dolomitization involves the mixing of two different waters at equilibrium with calcium carbonate. Because the solubility curve for calcite is non-linear (Fig. 22) the mixing results in a third water that is undersaturated with respect to calcite and capable of dolomitization (Fig. 24). Runnels (1969) suggests the same principle can be applied to other minerals with non-linear solubility functions. I therefore believe mixing of two different waters saturated with respect to silica will result in a supersaturated water that should precipitate silica (Fig. 23).

Percolating fresh water (ph 5.6-7) through subaerially exposed carbonate rocks and mixing it with sea water in the pores in the rocks will result in dolomitization, silicification, and ferric iron precipitation (Fig. 25). Ferric iron in slightly acidic solutions will precipitate on carbonate minerals due to increased

Figure 24. Mixing of 5-30% sea water with 95-70% fresh water results in a solution which is supersaturated with respect to dolomite and undersaturated with respect to calcite. This solution should result in dolomitization. From Badiozamani, 1973.

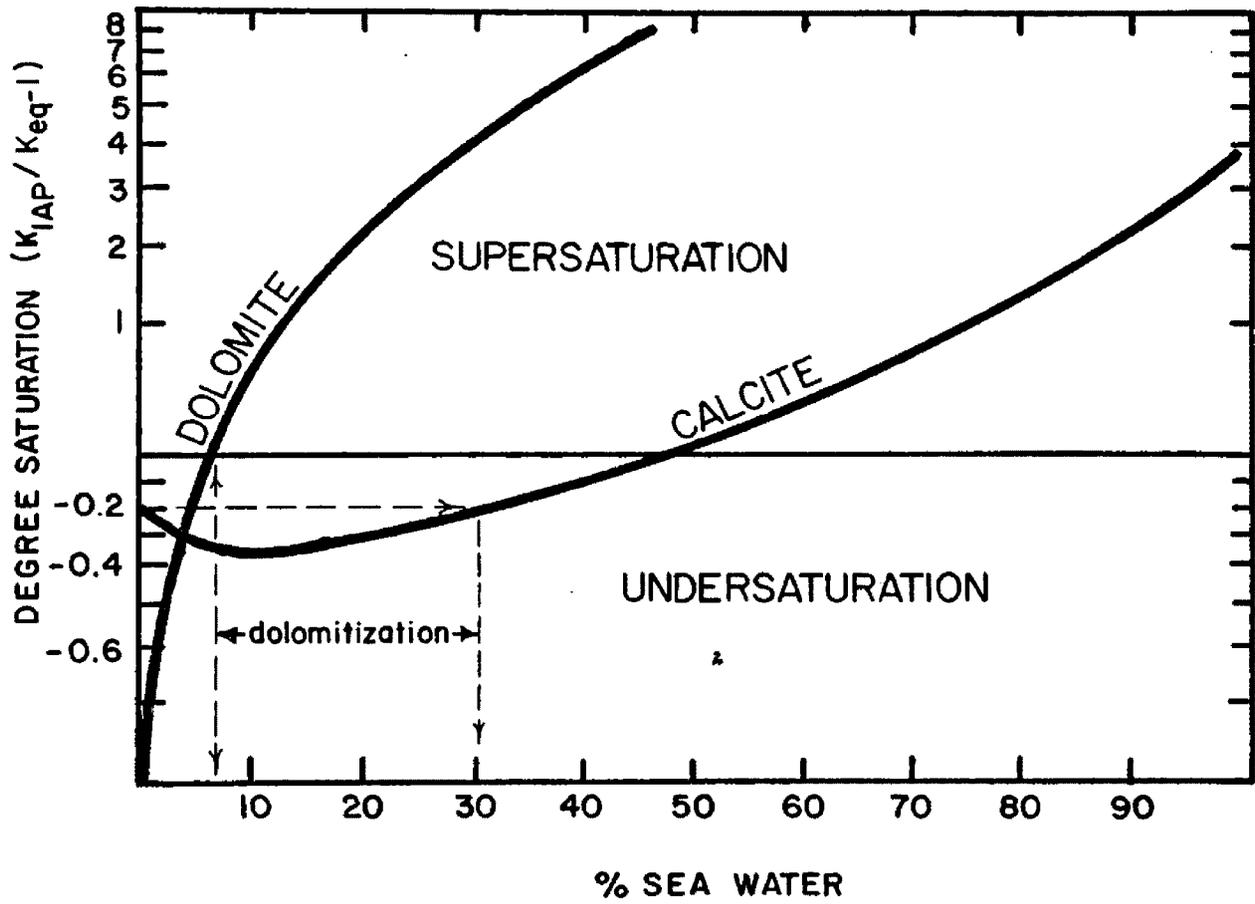


FIGURE 24 after Badiozamani, 1973

alkalinity (Fig. 13). Water percolated through the subaerially exposed carbonate rocks becomes more alkaline (pH 8.0-11) and capable of dissolving silica in the underlying sandstones and granites (Fig. 14), producing a water saturated with respect to silica. In a similar way sea water in the pore spaces of the rocks could also become saturated with respect to silica. Mixing the two waters would result in silicification and dolomitization.

Uplift along the Ute Pass Fault Zone during the post-Manitou Pre-Devonian hiatus resulted in weathering at the Indian Trail Locality (Fig. 25). This weathering following the previously described model would produce a red pervasive dolomite with abundant chert. Silica derived from solution of the underlying Cambrian sandstones and Precambrian granites would be precipitated on the E-4 nodules in the zone of mixing. Sea-level fluctuations, tectonic uplift and/or variations in fresh water influx would move the fresh water - sea water boundary up and down through the rocks resulting in any number of alternating periods of silicification and dolomitization. Thus faulting and subaerial exposure of the Indian Trail Locality during the Lower Ordovician to Devonian hiatus resulted in the influx of fresh water which initiated the diagenetic dolomitization process, silicification and precipitation of ferric iron.

#### Episode 7 - Calcitization

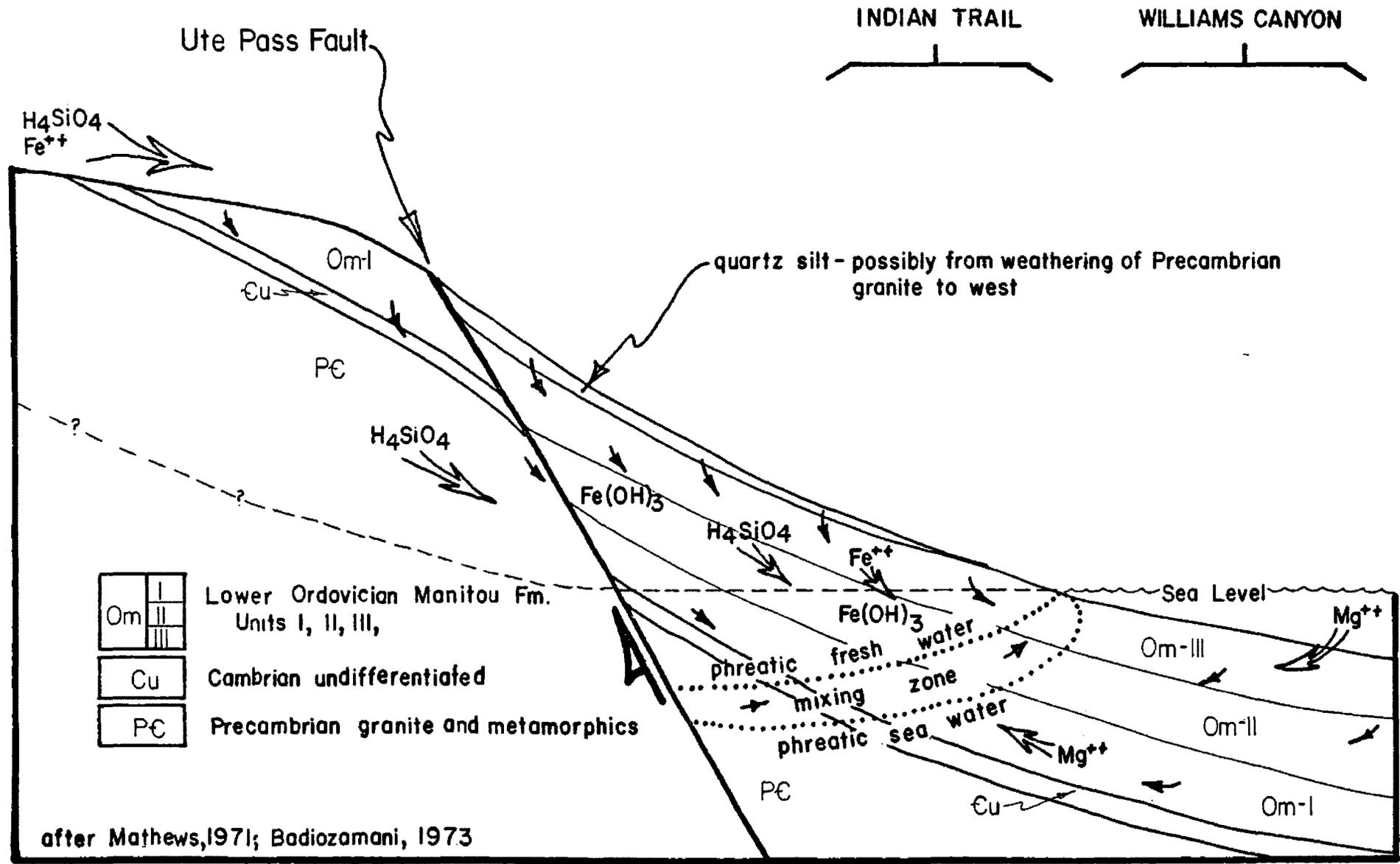
The last diagenetic episode to occur in the Manitou Formation was

Figure 25. Model for weathering resulting in dolomitization, silicification and solution along the Ute Pass Fault Zone. Influx of fresh water with dissolved iron from the west will result in solution of carbonate minerals increasing the alkalinity and precipitating ferric iron,  $\text{Fe}(\text{OH})_3$ . Alkaline water in the pore fluids of the carbonate rocks will percolate down into the underlying siliceous Cambrian and Precambrian rocks. Those fluids will become saturated with respect to silica. Silica and dolomite will then be precipitated in the zone of mixing due to the *mischungskorrosion* effect (page 59, text). Magnesium required for dolomitization is derived from sea water. The approximate locations of Indian Trail and Williams Canyon are indicated.

FIGURE 25

WEST

EAST



Om	I	Lower Ordovician Manitou Fm. Units I, II, III,
Cu		
PC		

Cu Cambrian undifferentiated  
PC Precambrian granite and metamorphics

after Mathews, 1971; Badiozamani, 1973

a period of calcitization that is more common at Williams Canyon than at Indian Trail. This is a clear calcite that in hand specimen obviously fills voids and fractures. Microscopically the calcite partly replaces silicified intraclasts and spicular cherts of E-4 and E-6a thus following E-6 in time (Fig. 20). This replacement is further evidenced by calcite truncating micrite quartz boundaries (Fig. 26 and 28) and has replaced E-6 dolomite rhombs (Fig. 27). The calcitization therefore occurred after the iron emplacement of E-6 and was therefore the latest diagenetic episode to occur in the Manitou Formation.

#### Summary of Diagenesis

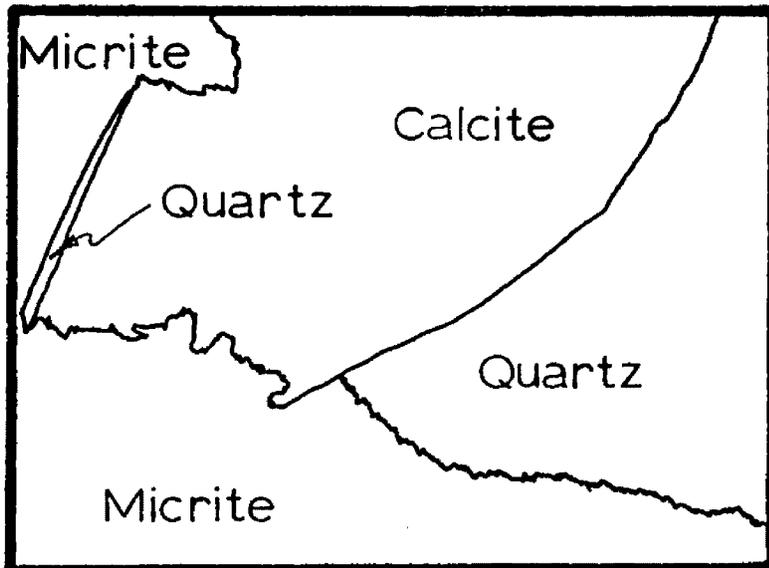
Individual beds in the Lower Ordovician Manitou Formation have gone through up to seven successive episodes of diagenesis. All of the episodes with the exception of E-6, occurred at both the Williams Canyon and Indian Trail Localities. Episode six occurred only at Indian Trail. These major episodes can be summarized as follows:

E-1 Cementation. Early calcite cementation of the sediments formed hardgrounds and partially lithified most of the sediments. This cementation occurred shortly after disposition.

E-2 Solution. Solution of the partially indurated limestone just below the mud-water interface resulted in two distinctive types of rock; 1) thin bedded and 2) lacy limestone.



FIGURE

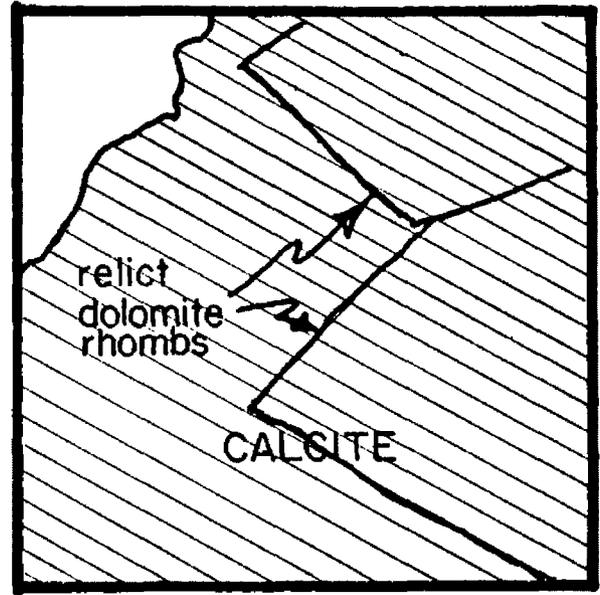


FIGURE

**FIGURE 26.** Calcite truncates the micrite-quartz boundary. The quartz grains are coarser away from the micrite indicating void filling quartz, but the calcite cuts across this grain size variation. The calcite therefore replaced both the micrite and the quartz.

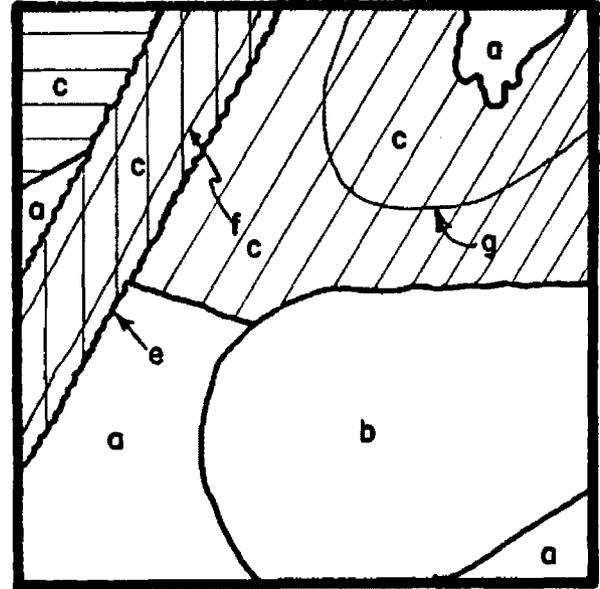
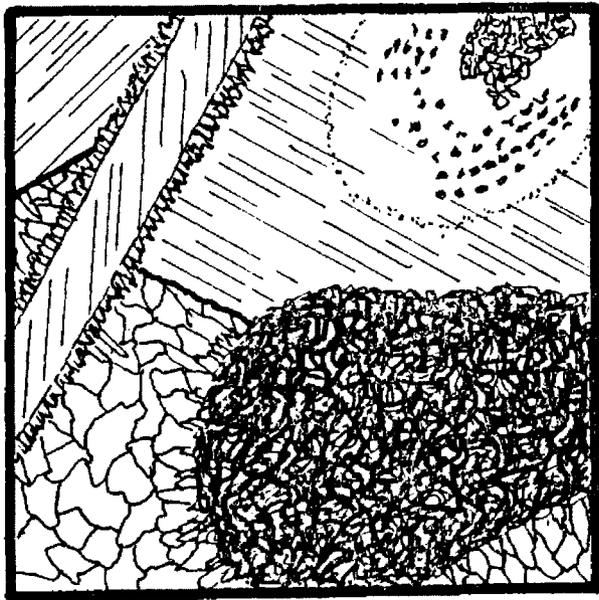
Figure 27. Relict zoned dolomite rhombs in calcite. Striped area shows extent of optically continuous calcite crystal.

Figure 28. Calcite-Silica-Micrite relationship.  
(a) E-4 Granoblastic quartz; (b) Micrite;  
(c) E-7 Calcite (Striped areas show individual crystals); (e) #-1 Calcite cement precipitated on trilobite fragment (f):  
(g) partially silicified echinoderm fragment with E-7 calcite overgrowth. Note the absence of quartz seed crystals on the calcite overgrowth that truncates the quartz, E-1 calcite cement boundary and therefore occurred after the silicification. Thin section sequence of diagenesis is (1) deposition; (2) E-1 calcitization; (3) E-4 silicification; (4) E-7 calcitization.



0.05 mm

FIGURE 27



1.0 mm

FIGURE 28

E-3 Dolomitization. This dolomitization created sparse dolomite rhombs which do not obliterate any of the primary structures in the sediment.

E-4 Silicification. Silicification replaced and preserved carbonate allochems and resulted in granoblastic and chalcedonic cement. This episode produced chert nodules which parallel bedding and are concentrated in horizons which correlate throughout the area.

E-5 Dolomitization. Post silicification dolomitization obliterated some of the primary structures in the rocks. Dolomitization was controlled by porosity and while some beds were partially to completely dolomitized, stratigraphically adjacent beds remained pure limestone.

E-6 Weathering. Weathering resulted in dolomitization, silification and solution at the Indian Trail Locality. These three processes are difficult to separate petrologically and probably occurred simultaneously.

Dolomitization - 6a, resulted in pervasive dolomitization which obliterated most of the primary structures. Along with this dolomitization oxidized iron pervasively stained the rocks red. The iron was either carried in solution and deposited on the dolomite or was incorporated in the original dolomite lattice and freed by solution.

Silicification - 6b, resulted in chalcedonic rims on the E-4 nodules and completely silicifying the carbonate minerals in and around the E-4 nodules. Chalcedony is the dominant silica mineral but some granoblastic and drusy quartz was also precipitated.

Solution - 6c, resulted in carbonate breccias and sink holes in the upper portion of the Manitou Formation at Indian Trail.

E-7 Calcitization. This was the last major diagenetic episode in the Manitou Formation. Sparry calcite formed masks most of the minerals resulting from the previous episodes.

### Discussion

The step by step diagenesis of individual beds in the Manitou Formation is a simplification of what actually occurred. Many of the episodes occurred simultaneously, the most obvious being Episode six where solution, silicification and dolomitization all took place during weathering. Many of the initial five episodes of diagenesis also occurred simultaneously. For instance, in the same horizon calcite spicules float in silicified (E-4) micrite intraclasts and silicified sponge spicules (E-4) float in micrite (Figs. 12, 16 and 20). Presuming the original spicules were aragonite, the simplest explanation for this diagenetic anomaly is that silicification occurred simultaneously with the transformation of aragonite to calcite.

Aragonite is the least stable carbonate mineral with respect to acidic solutions and micrite is less stable than a calcite spicule due to the increased surface area of the crystals in the micrite. An acidic solution capable of silicification would replace the aragonitic spicule easiest, the micrite next and the calcite would be the least susceptible of the three to silicification. If a limited amount of acidic solution is available, the replacement of carbonate by silica would result in neutralization of the acidic solution, thereby stopping the reaction prior to total silicification. Simultaneous silicification and transformation of aragonite to calcite could thereby result in silicification of aragonite spicules and not the surrounding micrite or where the aragonite spicules have recrystallized to calcite the micrite may be preferentially silicified.

The simultaneous occurrence of calcitization and silicification requires that E-1 and E-4 overlapped in time, and therefore E-2 and E-3 had to have overlapped with E-1 and/or E-4. It might be reasonable to hypothesize that the E-2 solution could have occurred with the E-4 silicification because both would require an acidic solution. However, silicified solution residues are rare and therefore the two processes probably did occur simultaneously. This means that E-1 may have overlapped with E-2.

The E-3 dolomitization and E-4 silicification may also have occurred simultaneously in that the E-3 and E-5 dolomitizations

could be combined into a single process which was interrupted by silicification. The similar characteristics of the two dolomitizations may suggest they are the result of the same process (Figs. 10 and 11), however, I cannot conclusively document this proposal. It is a reasonable proposal in that it would simplify an otherwise complex diagenetic history.

Figure 29 graphically depicts what I believe to be the time relationships of the major episodes. This is a summary of the diagenesis and is in no way meant to draw distinct boundaries defining a beginning and an end to each episode. Instead it shows what the majority of the petrologic evidence suggests about the relationship of the episodes.

Episodes one through five apparently occurred just below the mud-water interface because they are closely related to E-2 solution which definitely occurred just below the mud-water interface. This requires simultaneous post-depositional occurrences of the diagenetic episodes as a result of localized solutions capable of dolomitizing, silicifying, and dissolving the limestone.

Most diagenetic processes have traditionally been thought to occur well after deposition as a result of a dolomitizing or silicifying solution percolating through the rocks (Swett, 1964; Banks, 1962 and others). Diagenetic sequences proposed for these types of processes can be clearly separated into distinct time defined

Figure 29. Time relationships of the major diagenetic episodes. Blackened circles indicate good evidence for initiation or termination. Hollow circle indicates questionable boundary.

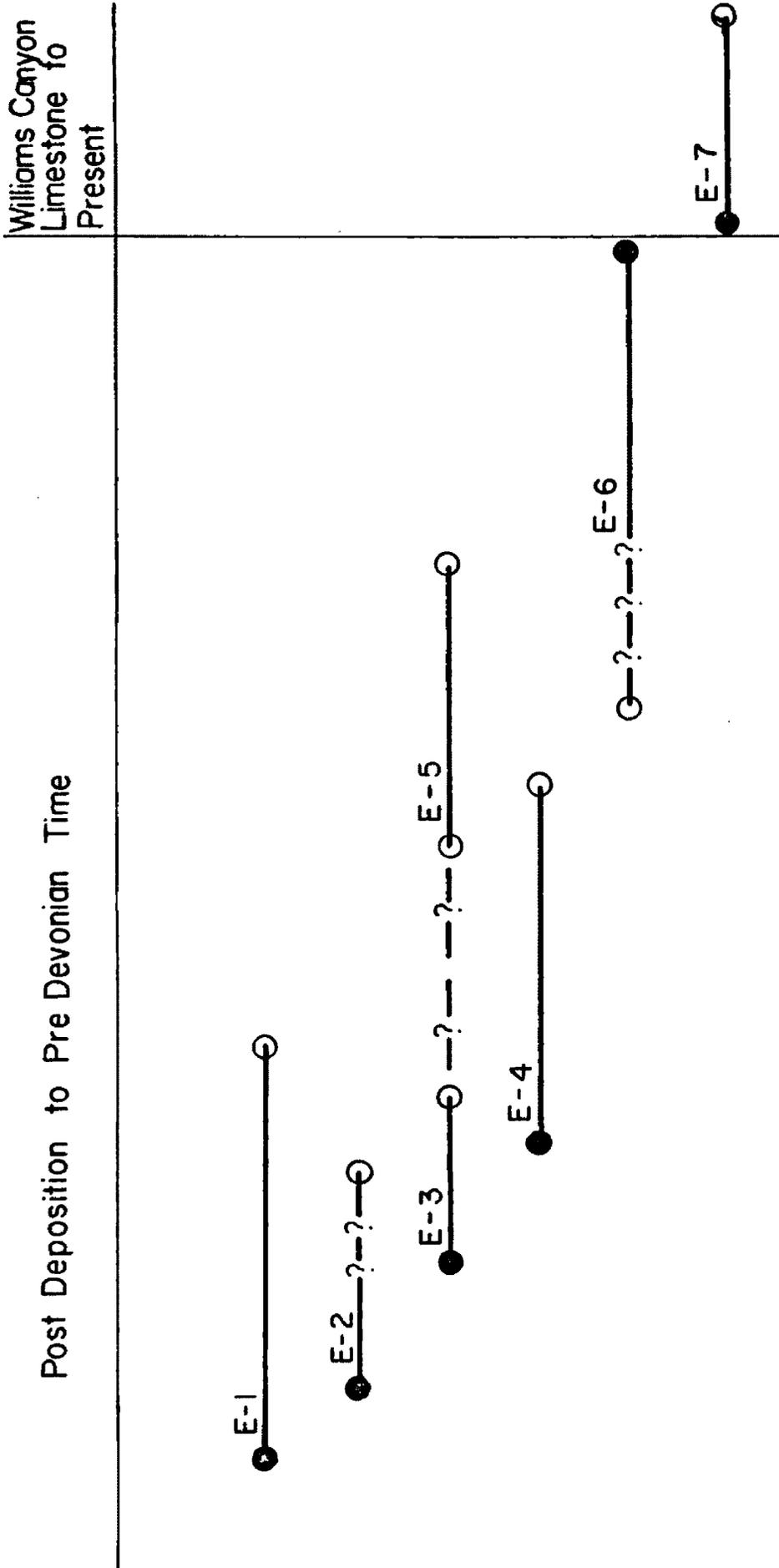


FIGURE 29

episodes that effected the entire unit or formation. However, the discrete step by step sequence of the diagenesis of the Manitou Formation is a simplification since some of the diagenetic processes occurred simultaneously (page 75, text). The simultaneous occurrence of two episodes does not infer that both diagenetic processes occurred in the same place during the same time interval. Instead, the simultaneous occurrence of two episodes refers to two or more localized processes taking place adjacent to one another.

This changes the traditional breakdown of the diagenesis into time defined episodes. Instead the diagenesis can be discussed in terms of processes, many of which overlapped in time. Some of these processes (E-1, E-2 and E-3) probably took place at a unique depth below the mud-water interface, possibly because of two factors: 1) depth of burial controlling reflux of sea-water through the uppermost sediments; and 2) organic decay locally controlling the pH. The E-1 cementation probably occurred within a few centimeters of the mud-water interface, E-2 solution also occurring at that depth and possibly a few centimeters deeper, and E-4 probably took place within a few meters of the interface but deep enough to allow a decreased pH. Continued deposition caused the lower occurring silicification rise, thereby replacing the minerals of the shallower processes.

Other processes such as the porosity controlled E-3 and E-5 dolomitizations were probably magnesium rich brines percolating down through the sediment during and after Episodes 1, 2 and 4. The

ultimate result is consistent replacement of one mineral by another. This replacement can be mistakenly broken down into the traditional diagenetic sequence of time defined episodes. Instead diagenetic episodes should be thought of as individual geochemical processes (i.e. silicification caused by organic decay locally lowering the pH in the sediments thereby precipitating silica).

## CHAPTER IV

### SUMMARY AND CONCLUSIONS

Six major episodes of diagenesis altered the rocks at both the Indian Trail and Williams Canyon Localities. These are E-1 cementation, E-2 solution, E-3 dolomitization, E-4 silicification, E-5 dolomitization and E-7 calcitization. With the exception of E-7 calcitization which is a late calcite, episodes one through five are the result of processes that continually took place during deposition. This simultaneous occurrence of the processes created minor replacements that do not fit in the above sequence.

These six major episodes are best seen at Williams Canyon where the Manitou Formation can be divided into three units on the basis of outcrop characteristics. Unit I, the basal unit is characterized by the thin bedded limestones created by the E-2 solution. Unit II is typified by the white bedded chert created by the E-4 solution. Unit III is characterized by the large alternating resistant and non-resistant beds of limestone and dolomite (E-5). A brief history including deposition and diagenesis of each unit will serve as a summary and should also indicate the major processes that created the outcrop characteristics of each unit at both localities.

Unit I was deposited mostly as micritic mud with occasional grainstone and packstone interbeds. Soon after deposition, calcite (?) cement (E-1) began to lithify the sediments. This was followed by solution (E-2) of the micrite immediately below the mud-water interface which created the thin bedded limestone that is characteristic of this unit. Following solution were episodes of dolomitization (E-3), silicification (E-4) and dolomitization (E-5). The two episodes of dolomitization which resulted in dolomitizing the more porous solution residues, grainstones and packstones, were probably the result of a single process of dolomitization which was interrupted by silicification. The E-3 silicification, which was restricted to the grainstones and packstones, preserved many of the primary structures of the original sediment.

Unit II is not characterized by bedded white chert nodules. At the time of deposition this unit was mudstone, grainstone and packstone with more grainstone and packstone beds than Unit I. Early cementation (E-1) and lithification were followed by solution (E-2) which created both thin bedded and the lacy limestones. This was followed by a minor dolomitization (E-3) which only partially dolomitized the sediments. This dolomitization was interrupted by silicification (E-4) which may reflect high concentrations of organic debris which in turn lowered the pH and precipitated bedded white chert nodules. Porosity controlled dolomitization (E-5) followed

silicification and in some beds obliterated the primary structures in the sediment.

Unit III is characterized by thick resistant limestone beds alternating with less resistant beds of dolomite. The original sediment in this unit was mostly micrite and algae with occasional allochems of many types. Following deposition, cementation (E-1) commonly created hardgrounds. Cementation was fairly complete in the limestone beds resulting in restriction of the dolomitizing solution to the more porous intervals. Solution (E-2) in this unit resulted mostly in lacy limestones but some of the dolomite beds appear to have been the thin bedded limestones. The dolomitization (E-3 and E-5) in this unit was clearly limited to the more porous beds. Dolomitization was again interrupted by silicification which created occasional chert nodules similar to the nodules that typify Unit II.

The sixth diagenetic episode to occur throughout the entire study area was a late calcitization. This calcitization replaces all of the previous diagenetic episodes with large clear calcite crystals. The calcitization was therefore the latest diagenetic episode to occur in the Manitou Formation.

Between episodes five and seven subaerial exposure of the Indian Trail Locality along the Ute Pass Fault Zone deeply weathered those rocks to a distinctive red color. This weathering (E-6) resulted in

pervasive dolomitization, silicification and solution. The dolomitization (E-6a) obliterated most of the primary constituents in the rocks that were not preserved by previous silicification. Silicification (E-6b) resulted in chalcedonic overgrowths on the previously formed E-4 chert nodules which served as nucleation sites for the later silicification. Solution (E-6c) in the upper portion of the section created sink holes and limestone breccias as well as oxidized iron producing the red color characteristic of the Indian Trail Locality. These three processes apparently resulted from the same episode since they are petrologically difficult to separate into a nice sequential order and because they are all unique to the Indian Trail Locality. A model similar to the Dorag model for dolomitization (Fig. 25), can account for the simultaneous occurrence of those three processes. In this model the mixing of fresh water and sea water saturated with respect to calcite, dolomite and amorphous silica creates a solution capable of dolomitization and silicification. The magnesium required for dolomitization is derived from the sea water. The influx of dissolved silica and iron in the fresh water provides the necessary elements for silicification and ferric iron deposition. This weathering occurred during the post-Manitou to Devonian hiatus because the overlying Devonian Williams Canyon Limestone is gray, indicating it was not subjected to the weathering.

## REFERENCES CITED

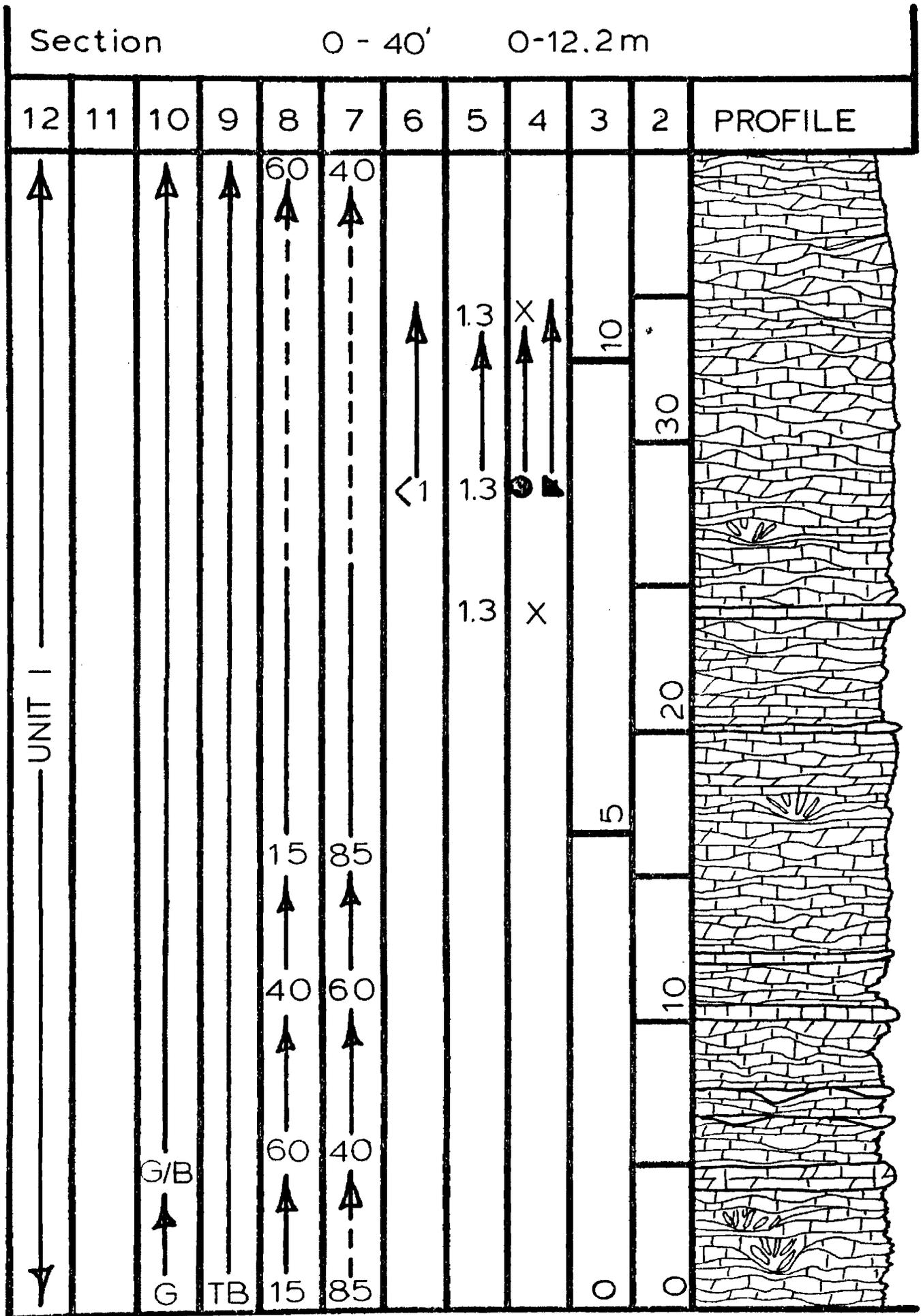
- Badiozamani, K., 1973, The Dorag dolomitization model-application to the Middle Ordovician of Wisconsin: Jour. Sed. Petrology, v. 43, p. 956-984.
- Banks, N.G., 1970, Nature and origin of early and late cherts in the Leadville Limestone, Colorado: Geol. Soc. Amer. Bull., v. 81, pt. 3, p. 3033.
- Bathurst, R.C., 1975, Carbonate Sediments and Their Diagenesis, Elsevier Scientific Publishing Co., New York, 658 pp.
- Cloud, P.E., Barnes, V.E., 1957, Early Ordovician Sea in Central Texas, in Treatise on Marine Ecology & Paleoecology, v. 2, H. S. Lodd (ed.), Geol. Soc. Amer. Memoir 67, pp. 163-214.
- Friedman, G. M., 1964, Early diagenesis and lithification in carbonate sediments, Jour. Sed. Petrology, v. 34, pp. 777-813.
- Krauskopf, K.B., 1967, Introduction to Geochemistry, McGraw-Hill Book Company, New York, 721 pp.
- Maher, J.C., 1950, Detailed sections of Pre-Pennsylvanian sediments along the Front Range of Colorado: U.S. Geol. Survey, Circular 68.
- Middleton, G., Blatt, J., and Murray, R., 1972, Origin of Sedimentary Rocks, Prentice-Hall Inc., New Jersey, 634 pp.
- Roehl, P. O., 1967, Strong mountain (Ordovician) and interlake (Silurian) facies analogs of recent low energy marine and subareal carbonates, Bahamas: Am. Assoc. Petroleum Geologist Bull., v. 51, pp. 1979-2031.
- Runnels, D.D., 1969, Diagenesis, chemical sediments and the mixing of natural waters: Jour. of Sed. Petrol., v. 37, pp. 1188-1201.
- Seiver, R., 1962, Silica solubility, 0-200°C, and the diagenesis of Siliceous Sediments: Jour. Geol., v. 70, p. 127-150.
- Swett, Keene, 1964, Petrology and paragenesis of the Ordovician Manitou Formation along the Front Range of Colorado: Jour. of Sed. Petrol., v. 34, no. 3, p. 615.

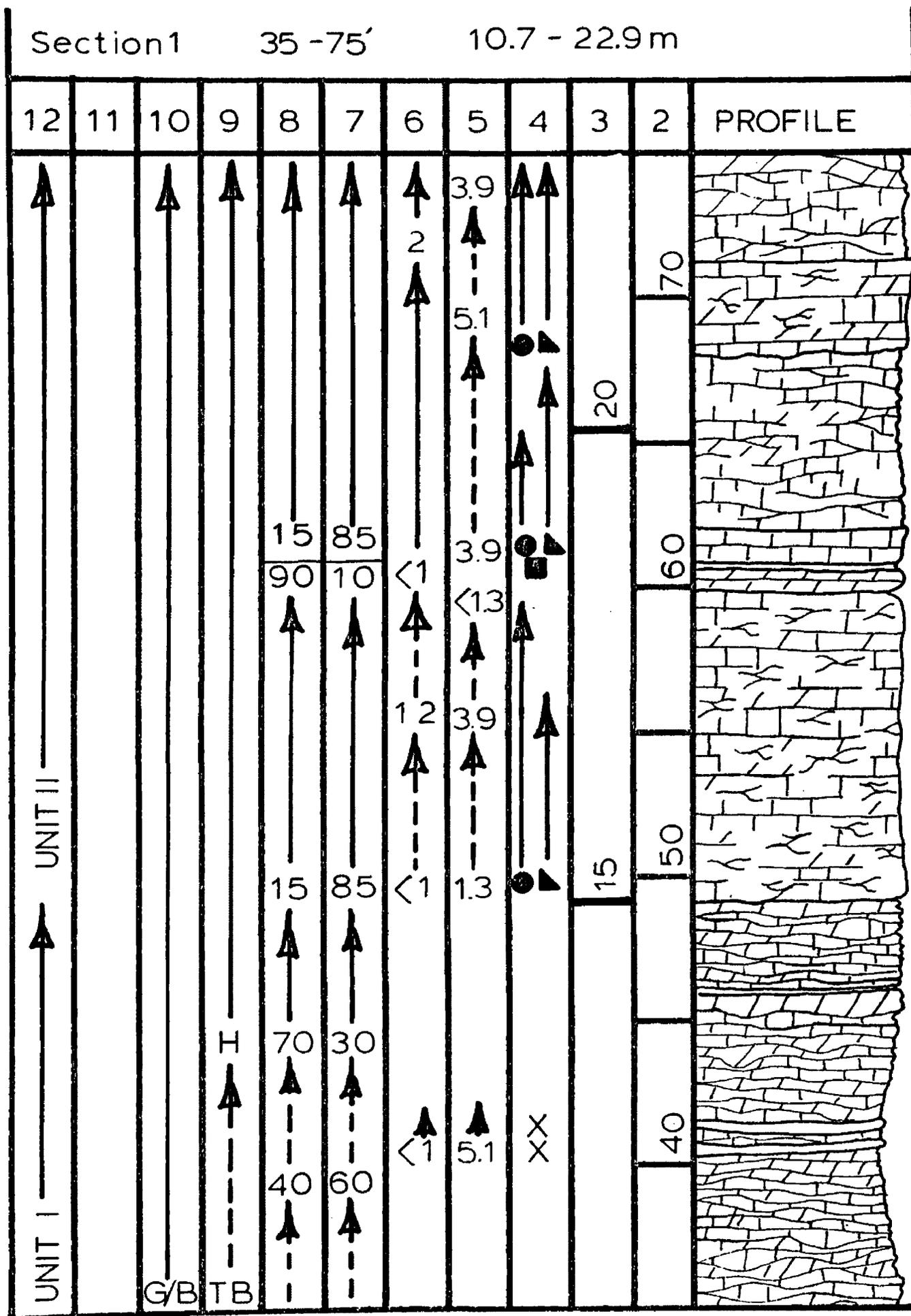
Walker, T. R., 1962, Reversible nature of chert-carbonate replacement in sedimentary rocks: Geol. Soc. America Bull., v. 73, p. 237.

## APPENDIX I

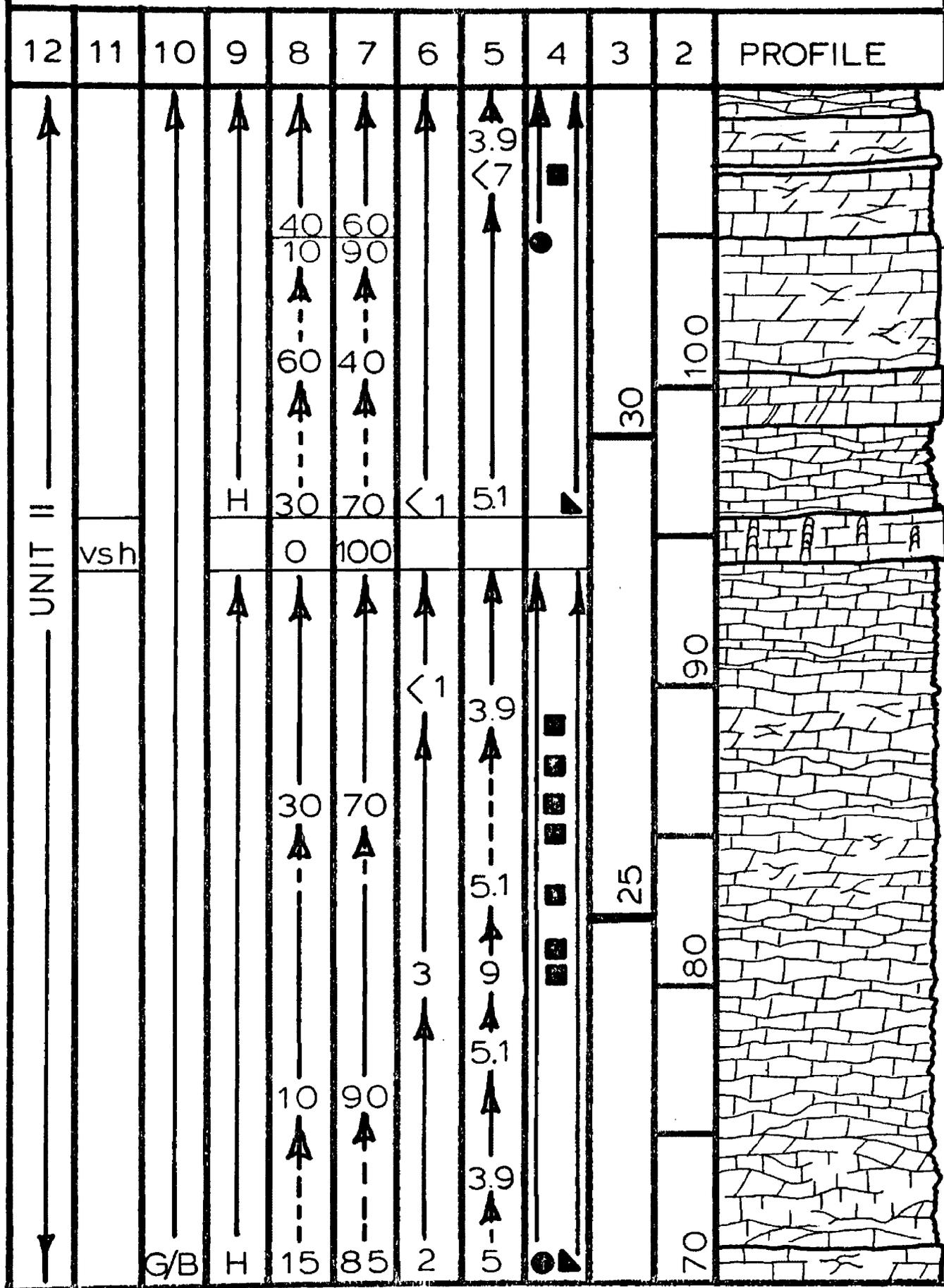
## MEASURED SECTIONS

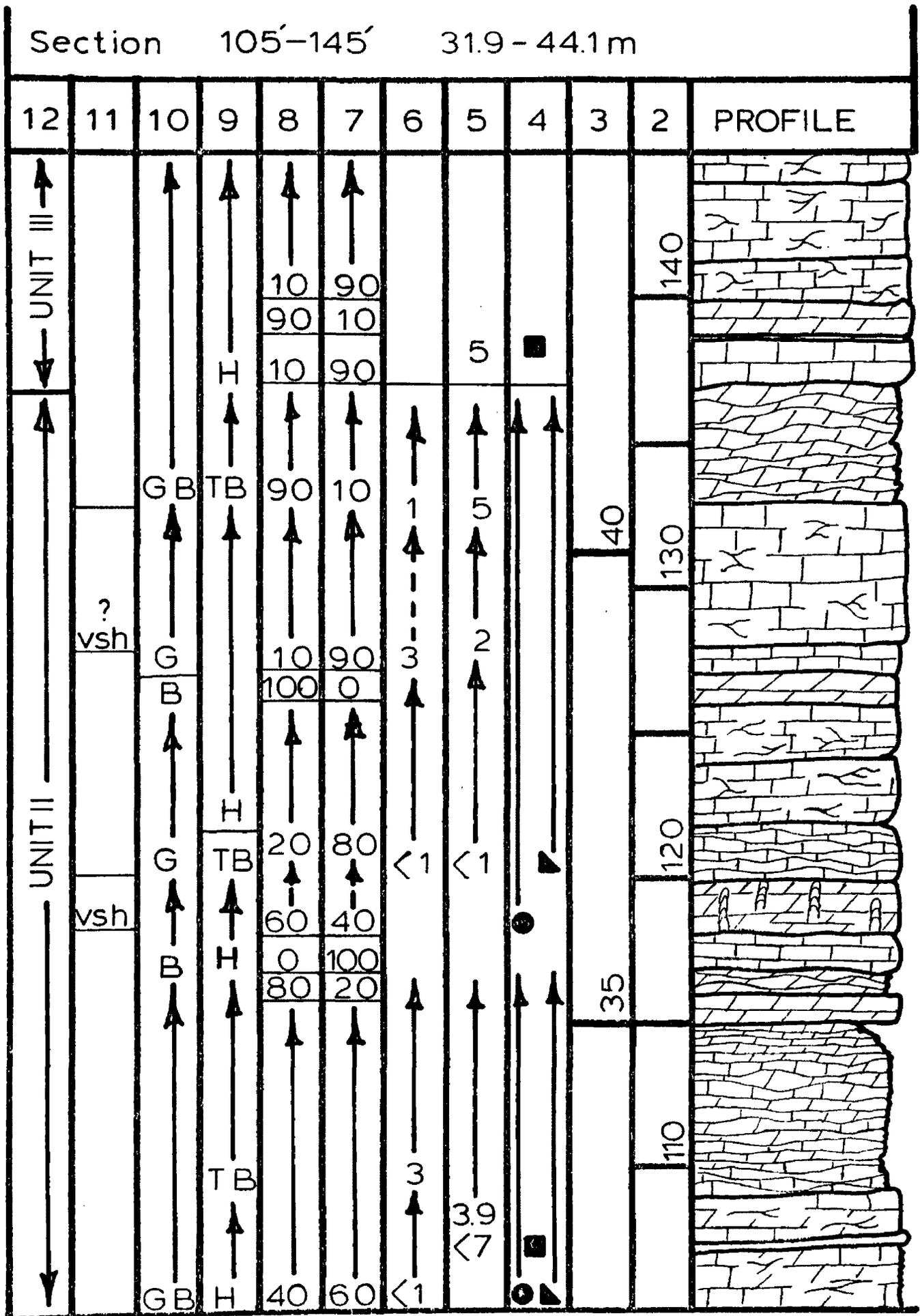
The measured sections are presented as stratigraphic columns with outcrop profiles, and tabulated in columns and are descriptions of the geology discernable in the field. From right to left the vertical columns are: 1) Profile of the stratigraphic columns; 2) Thickness in feet of the section from the base; 3) Thickness in meters from the base; 4) Outcrop characteristics of the chert:  = Nodular chert cutting bedding planes,  = Nodular cherts which delineate bedding,  = Continuous chert beds,  = silicified fossil fragments,  = Nonbedded disseminated chert (filagreed chert);  = Disseminated chert restricted to a limited vertical horizon; 5) Maximum thickness of a chert nodule or chert bed in centimeters; 6) Chert beds or nodules per vertical 0.3 meters; 7) Percentage of carbonate minerals that are limestone as determined in hand specimen; 8) Percentage of carbonate minerals that are dolomite as determined in hand specimen; 9) Nature of the dolomite, P = pervasively dolomitized rock, H = lacy disseminated wisps of dolomite, TB = dolomite interstitial to thin limestone nodules and beds; 10) Color of rock on a freshly broken surface, B = buff yellow, G = gray, R = red, N = brown; 11) Type of algae, M = matts, VSH = vertically stacked hemispheroids, LLH = laterally linked hemispheroids, SH = spherical hemispheroids; 12) correlation of the sections by units.

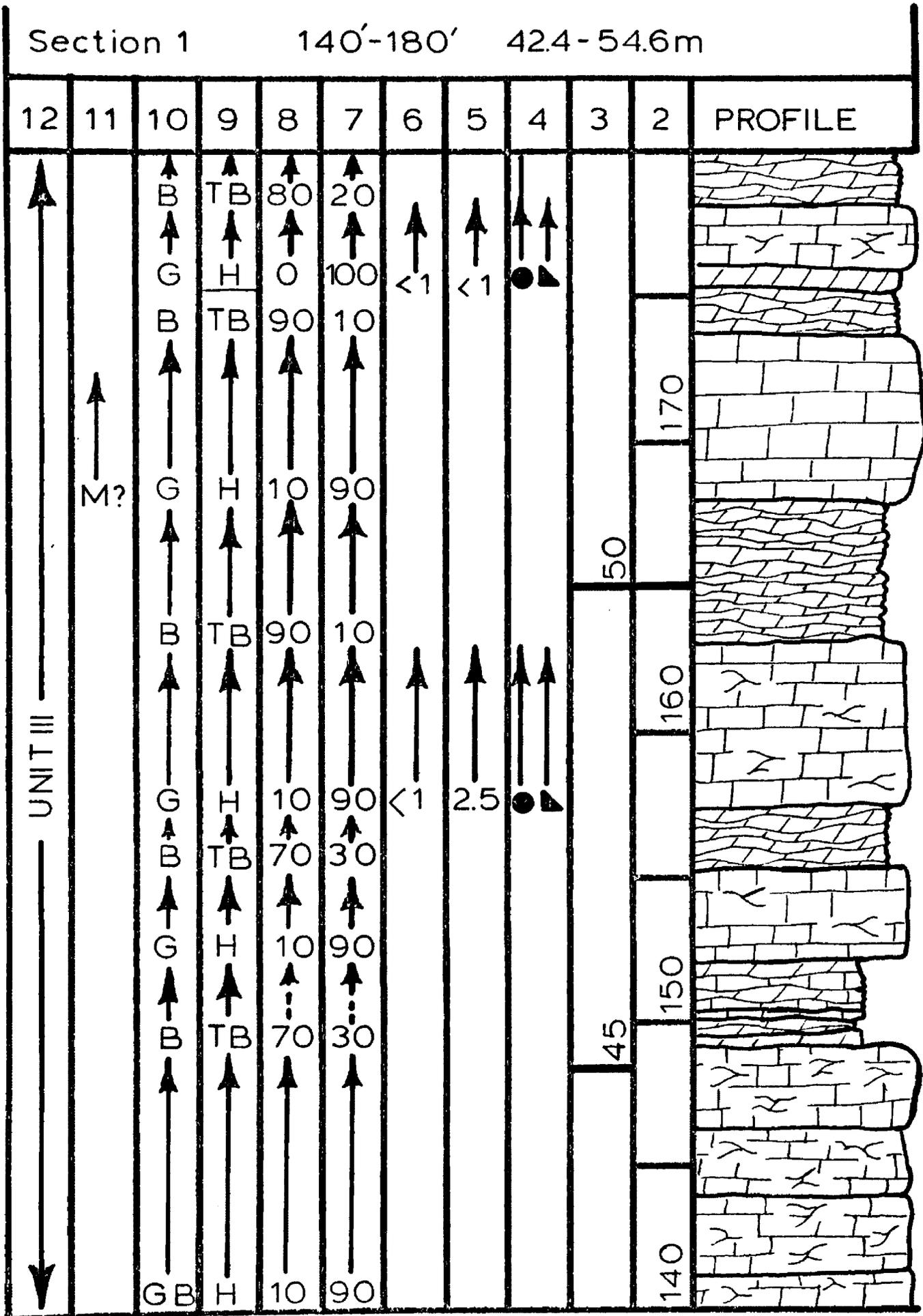


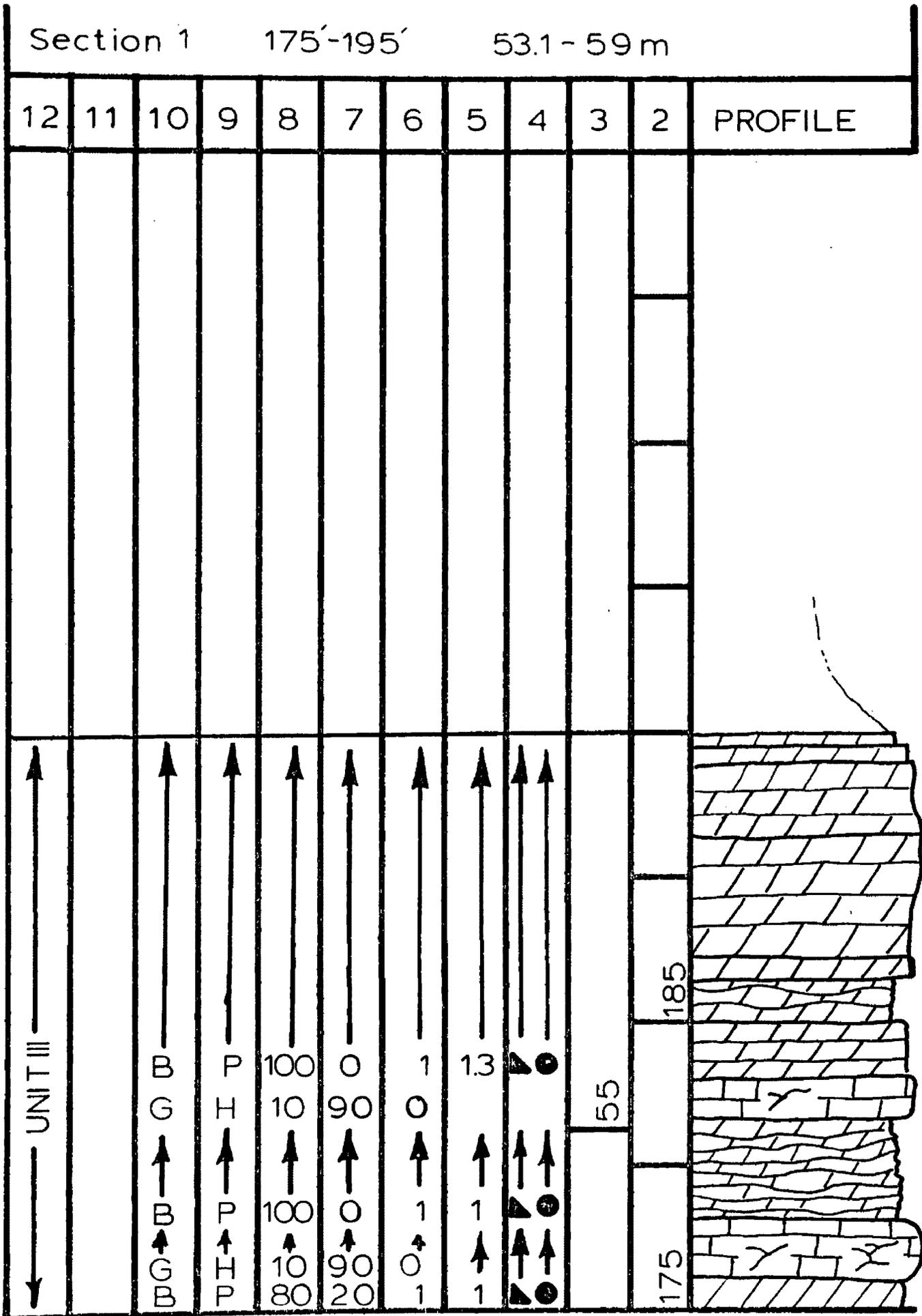


Section 1 70'-110' 21.4-33.6m





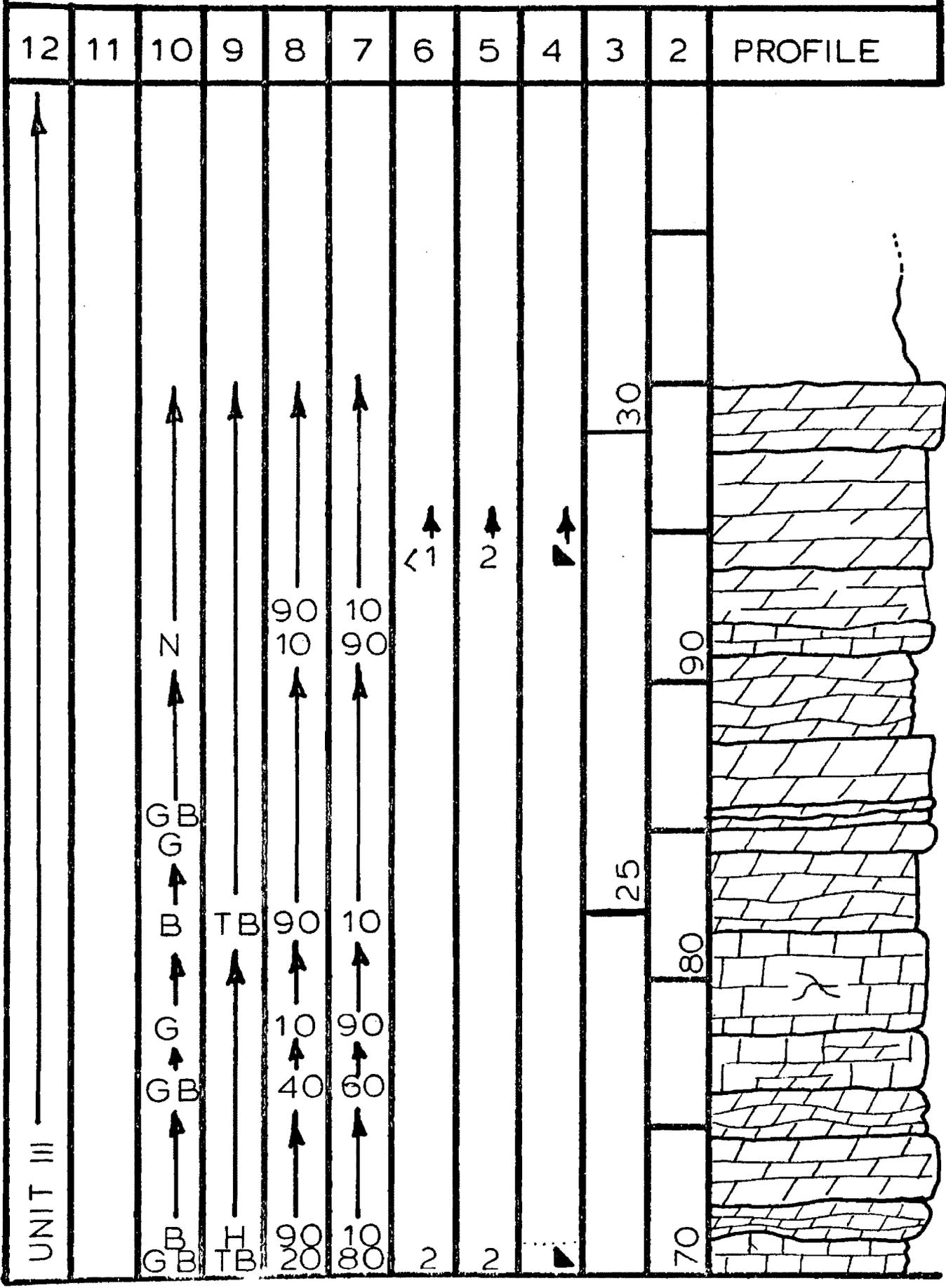




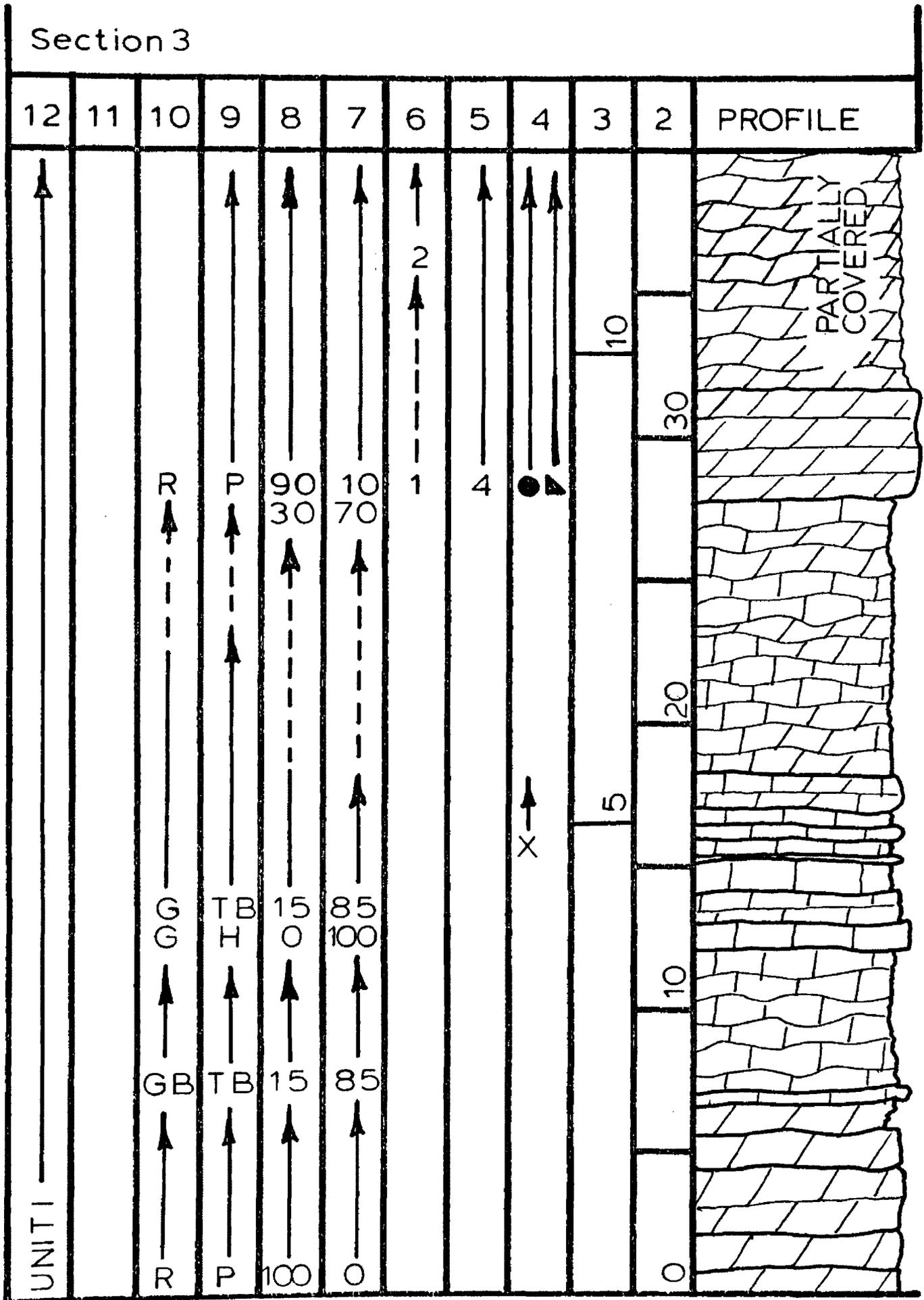




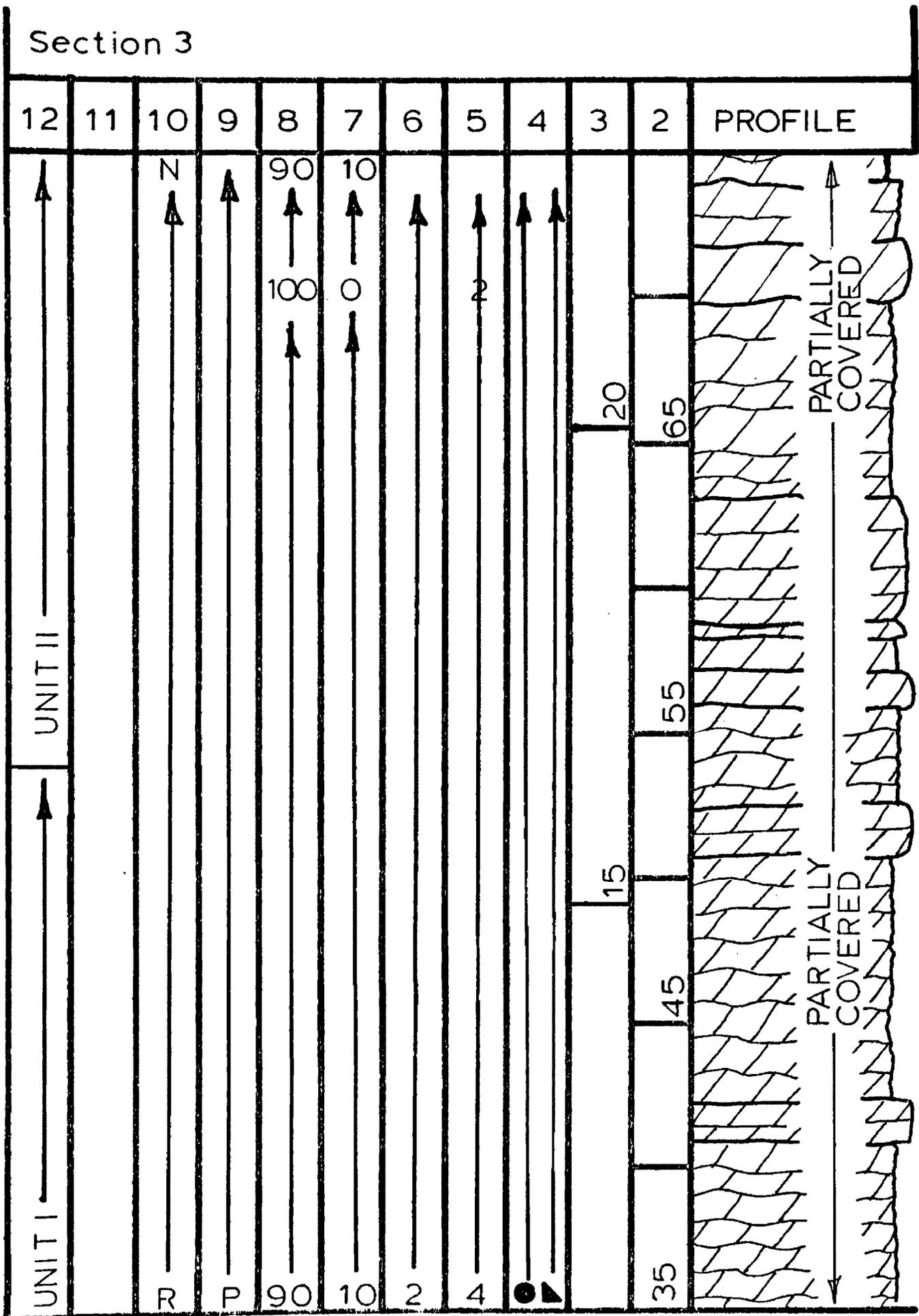
Section 2



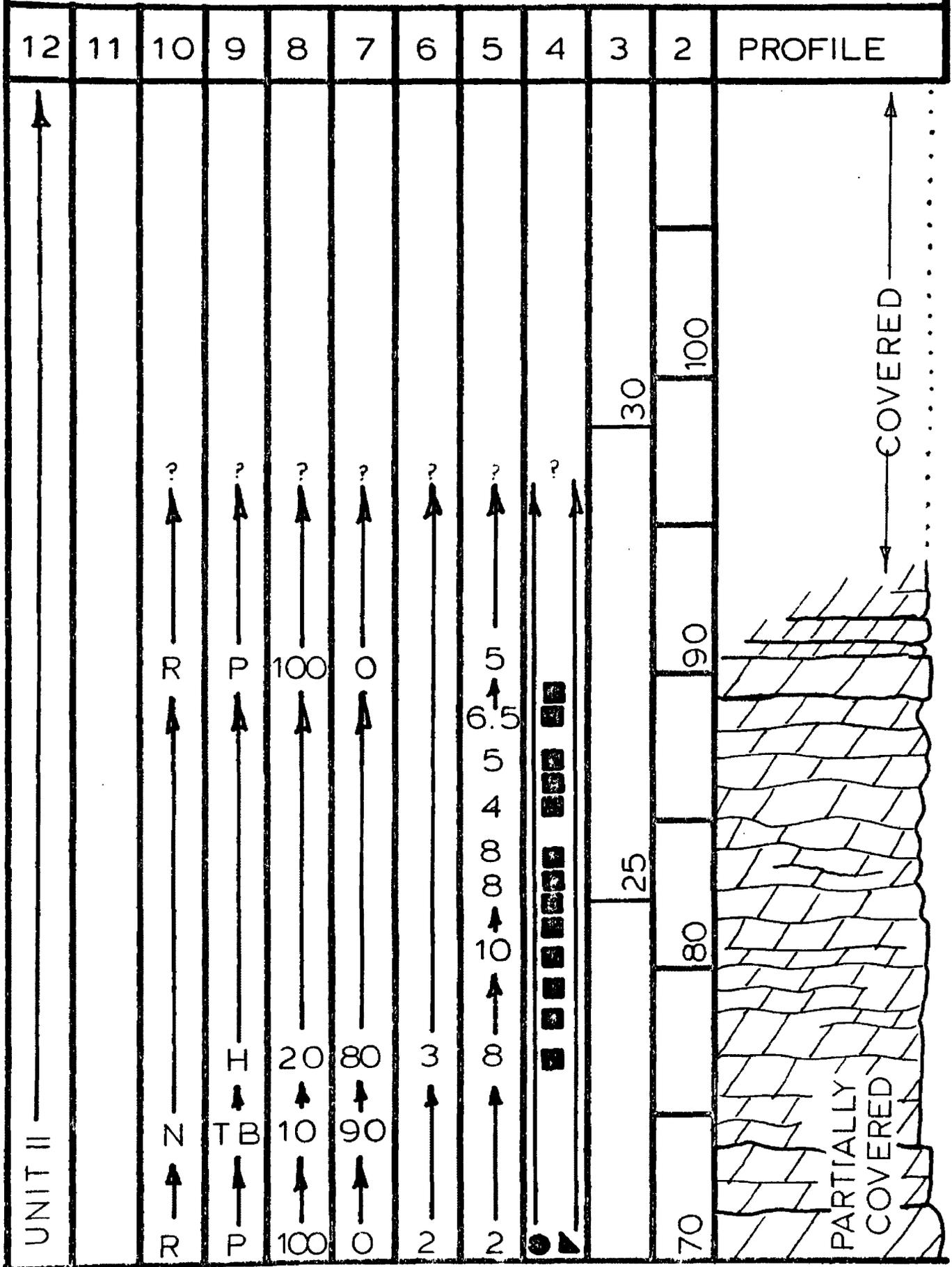
Section 3



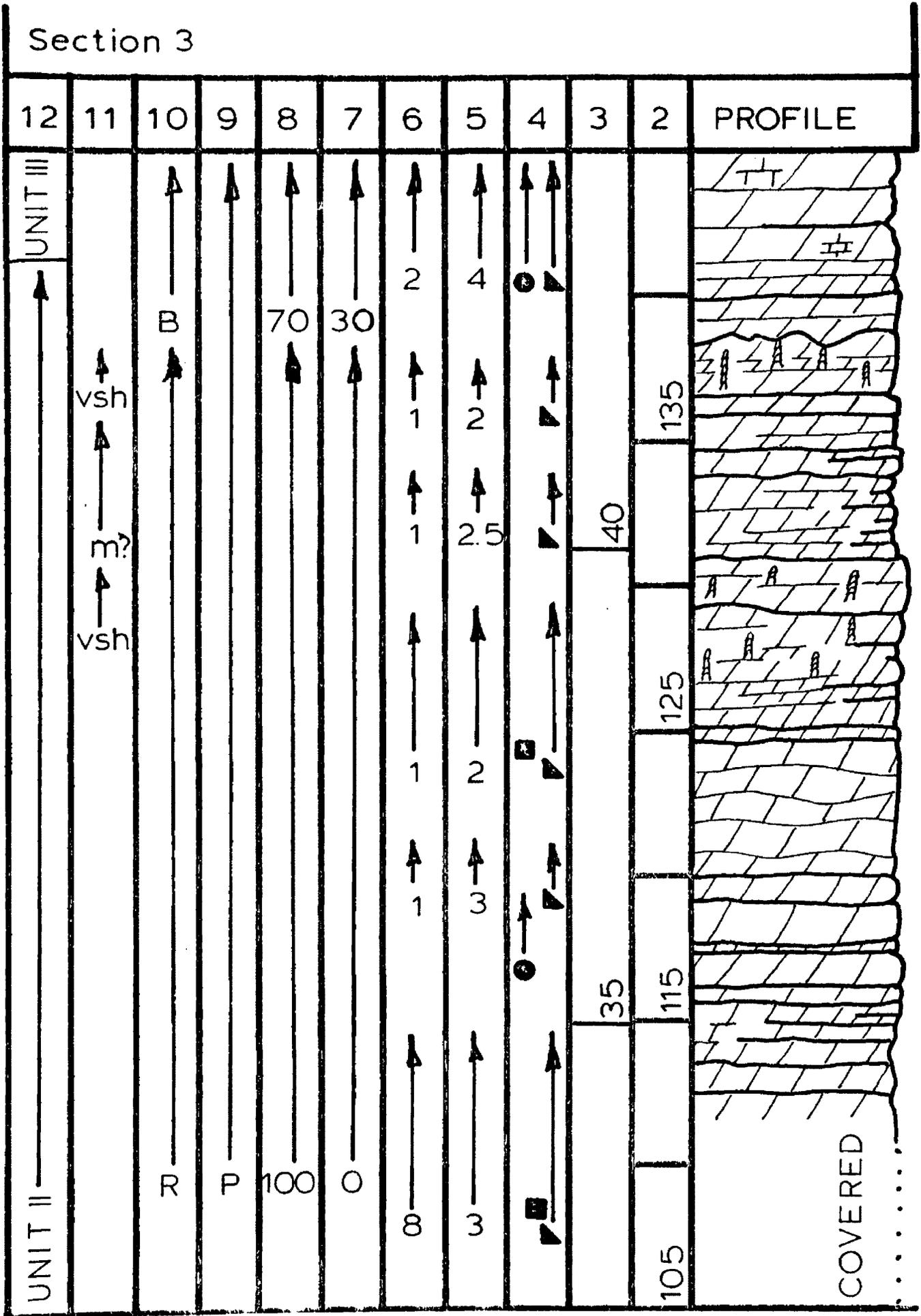
### Section 3

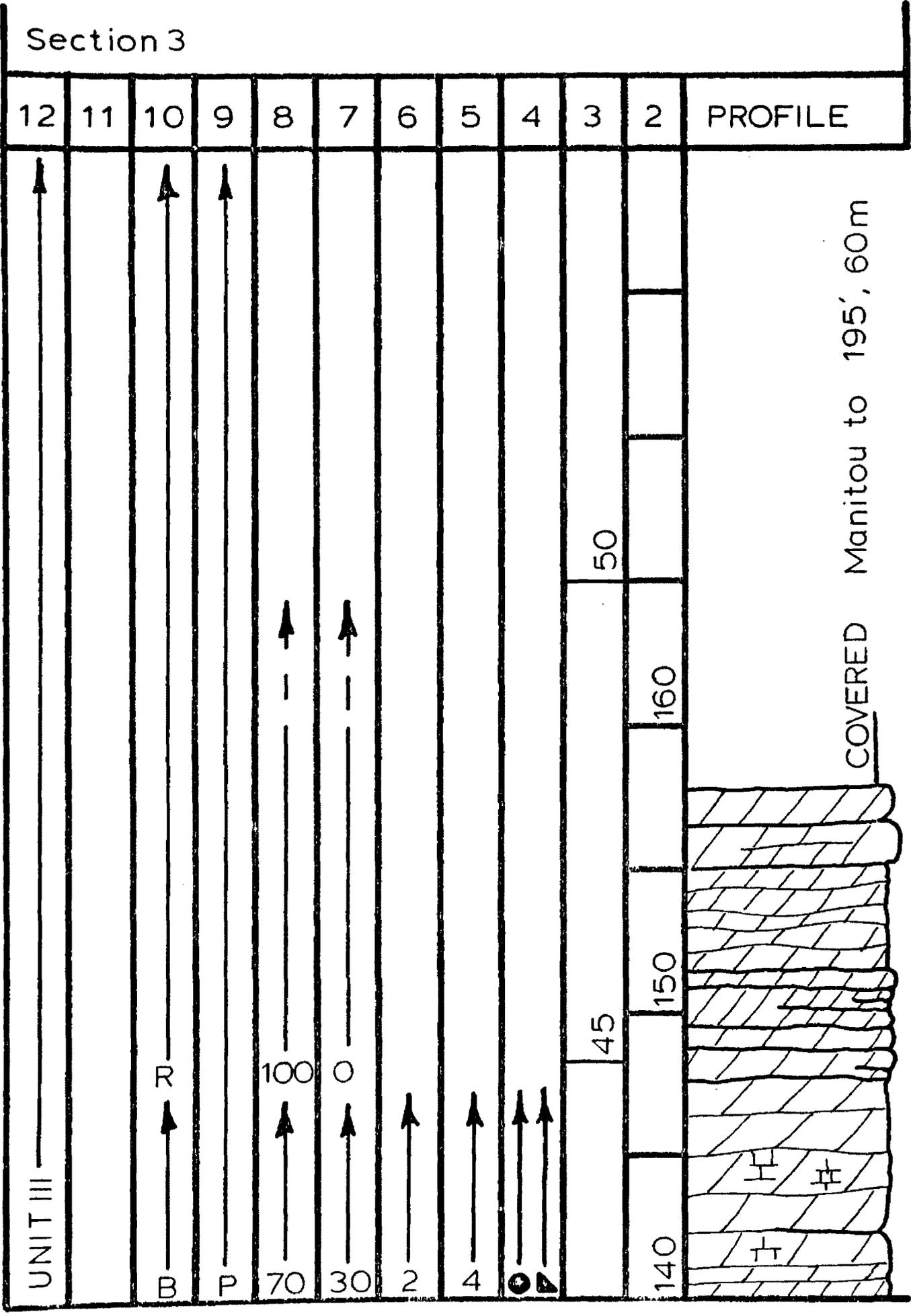


Section 3

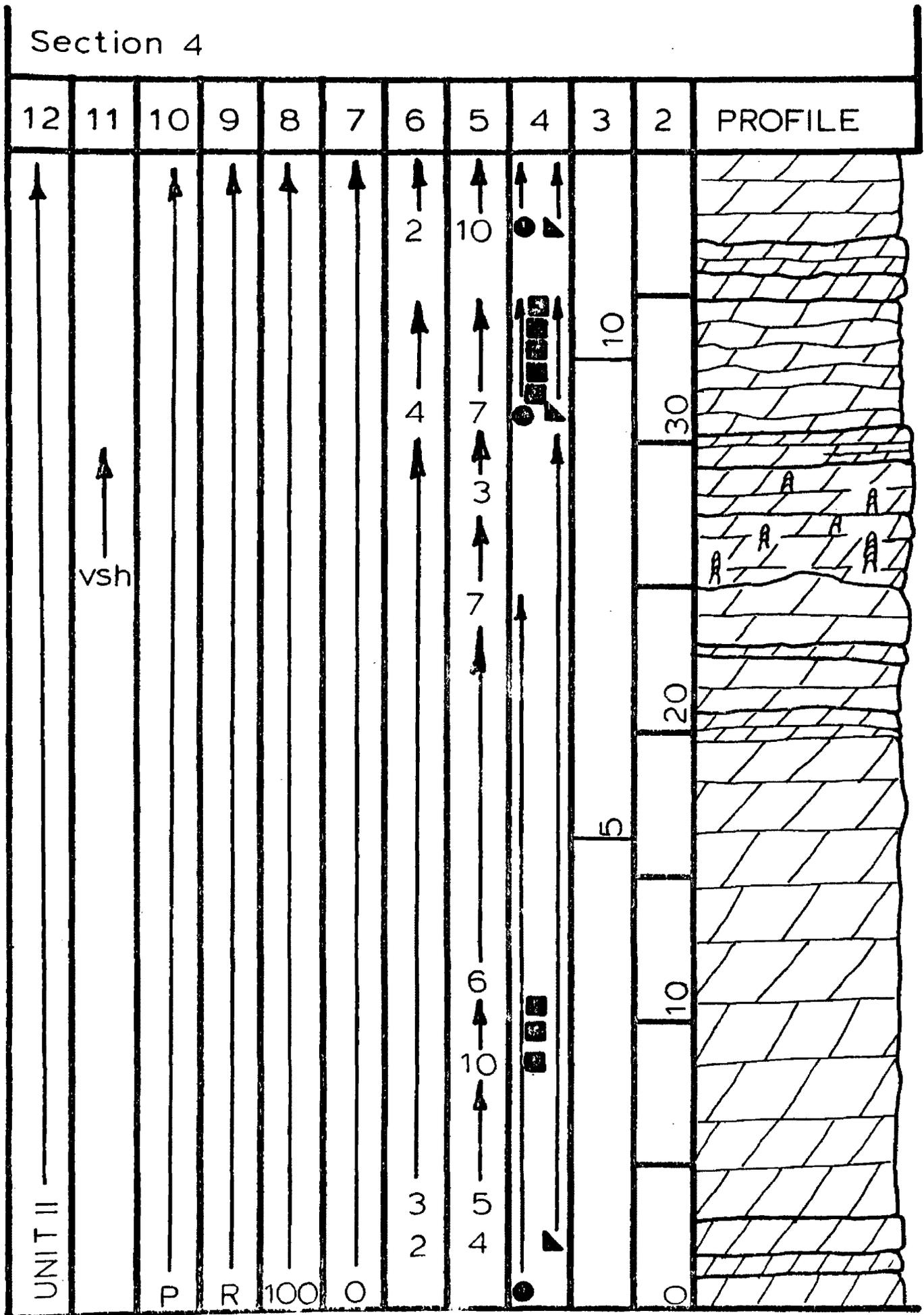


Section 3

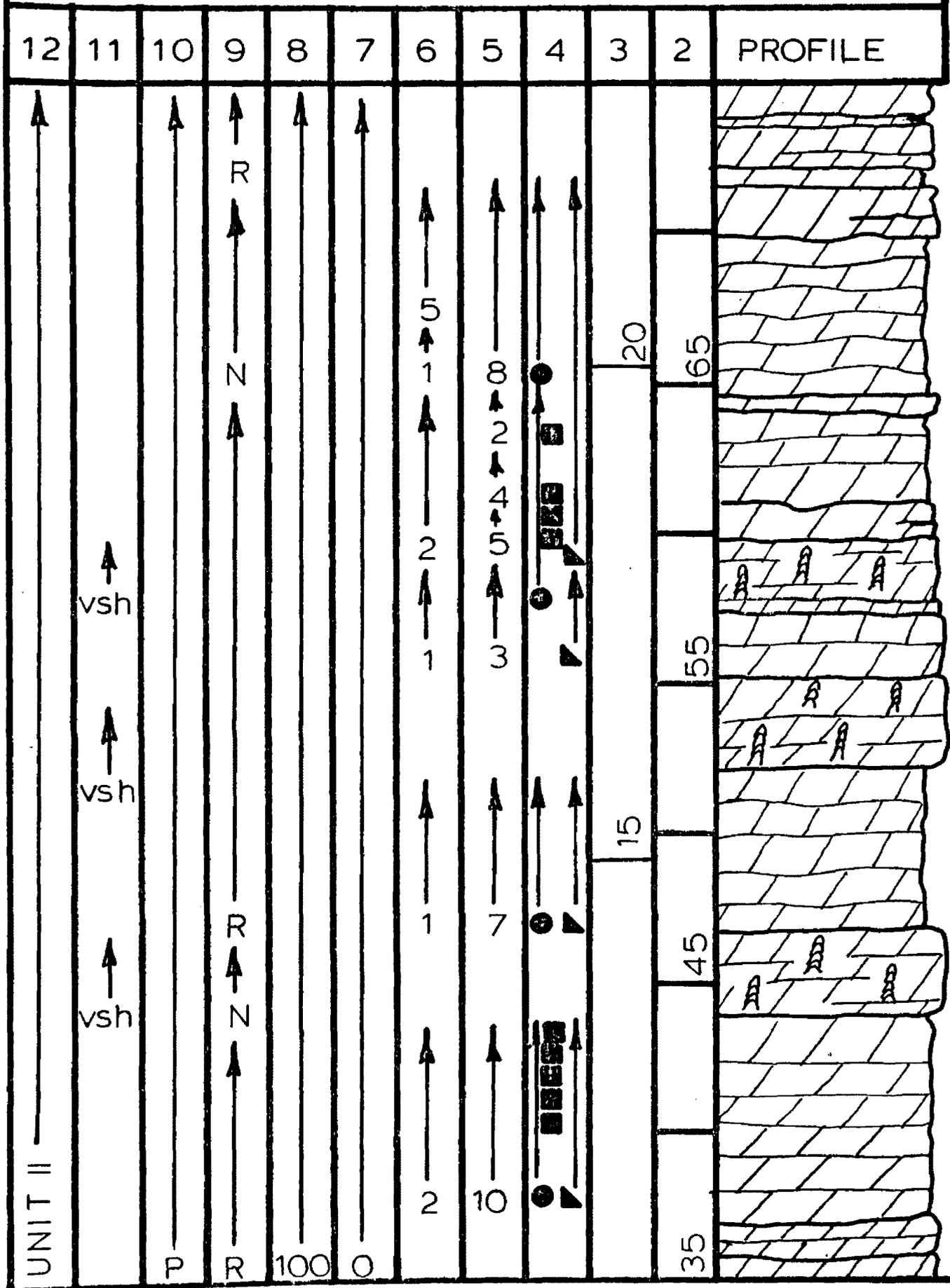




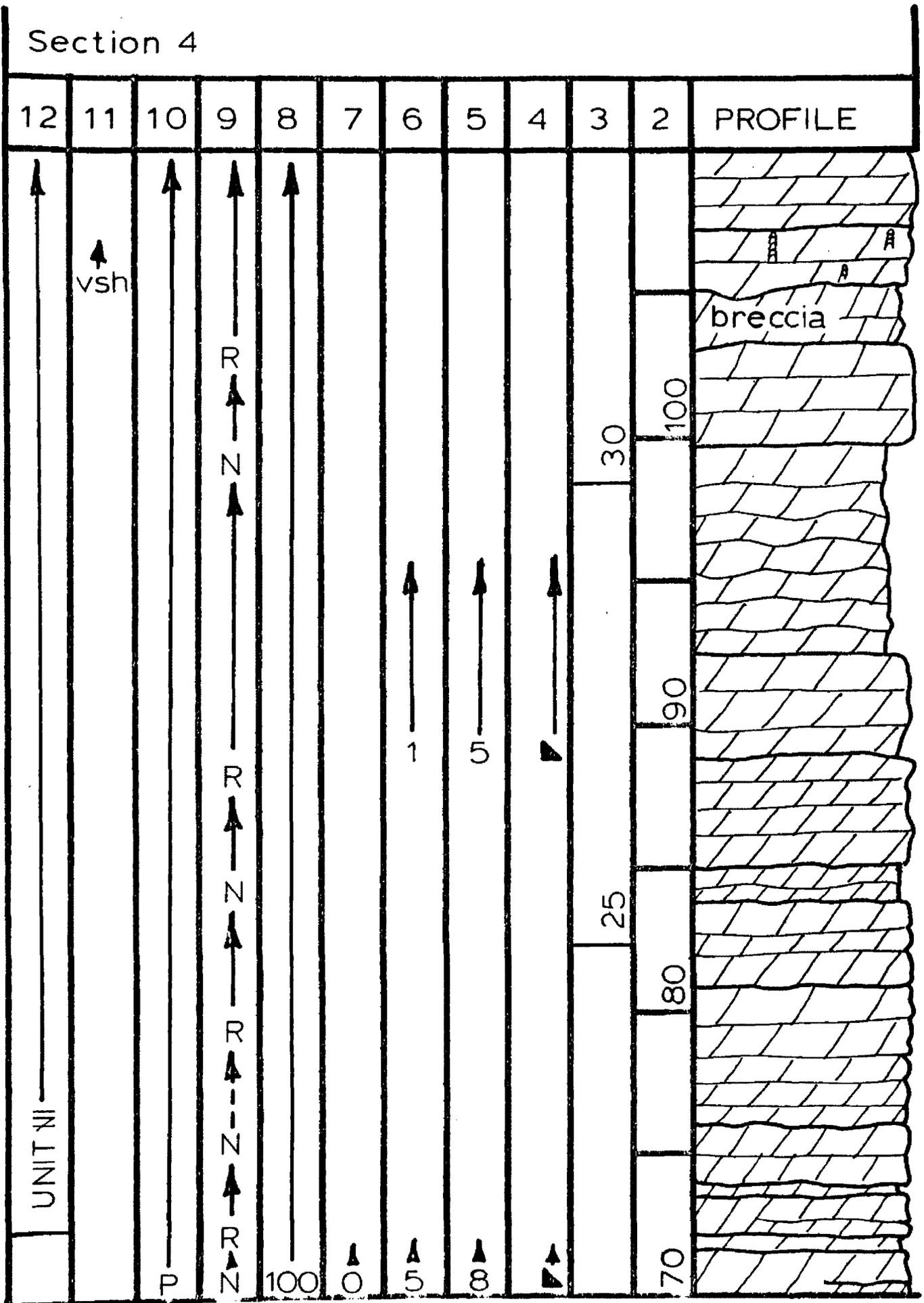
Section 4



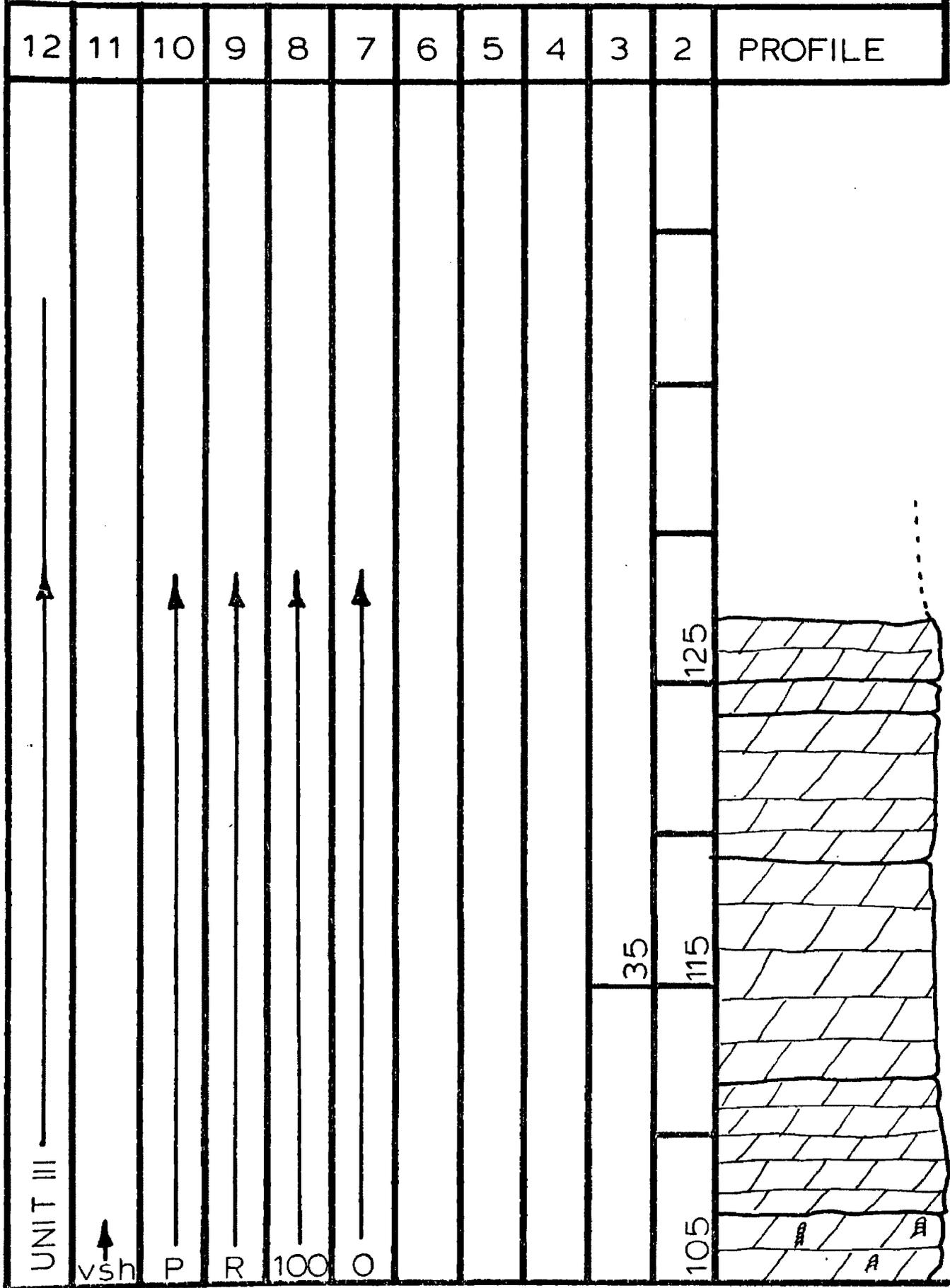
Section 4



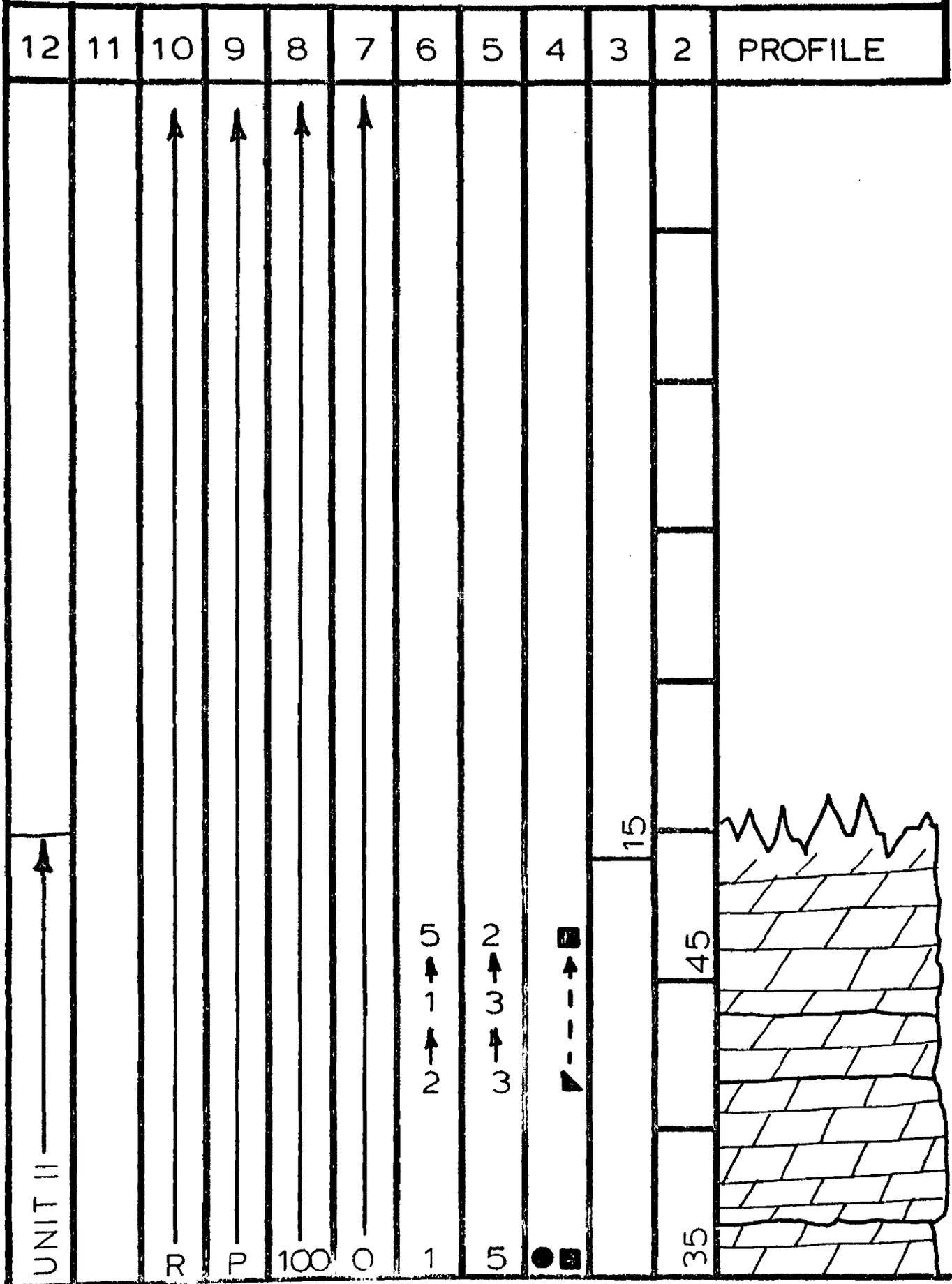
Section 4



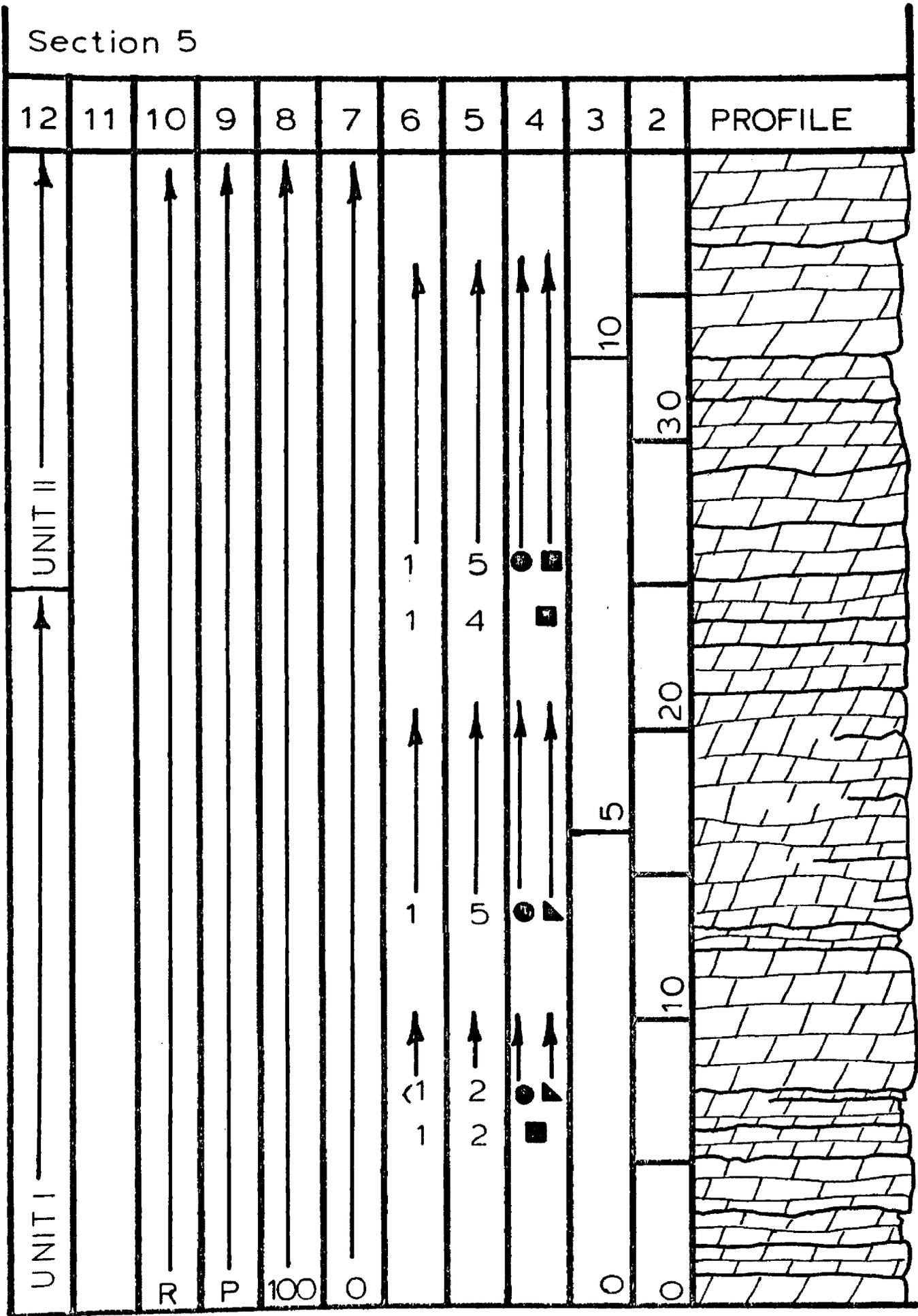
Section 4



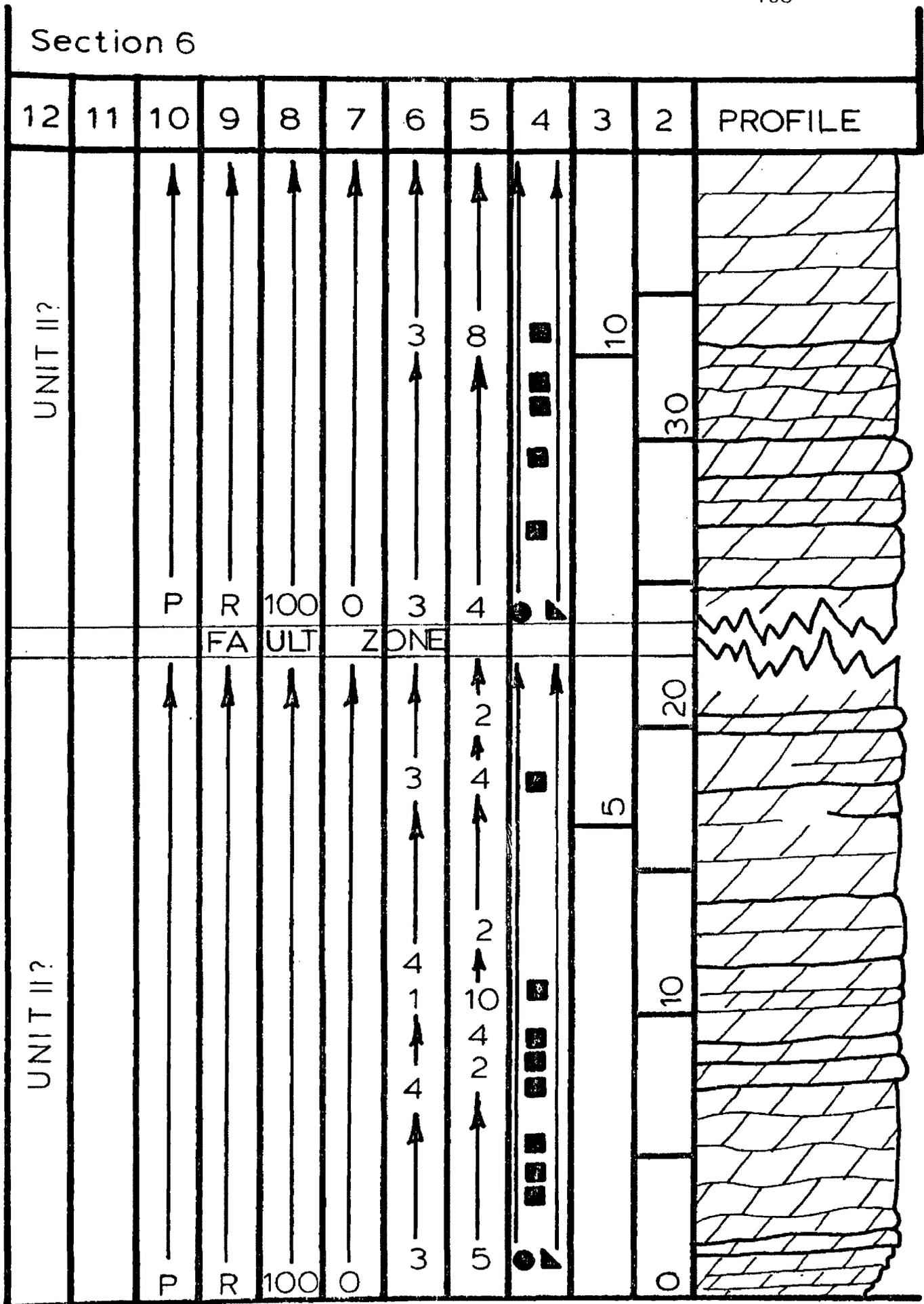
# Section 5



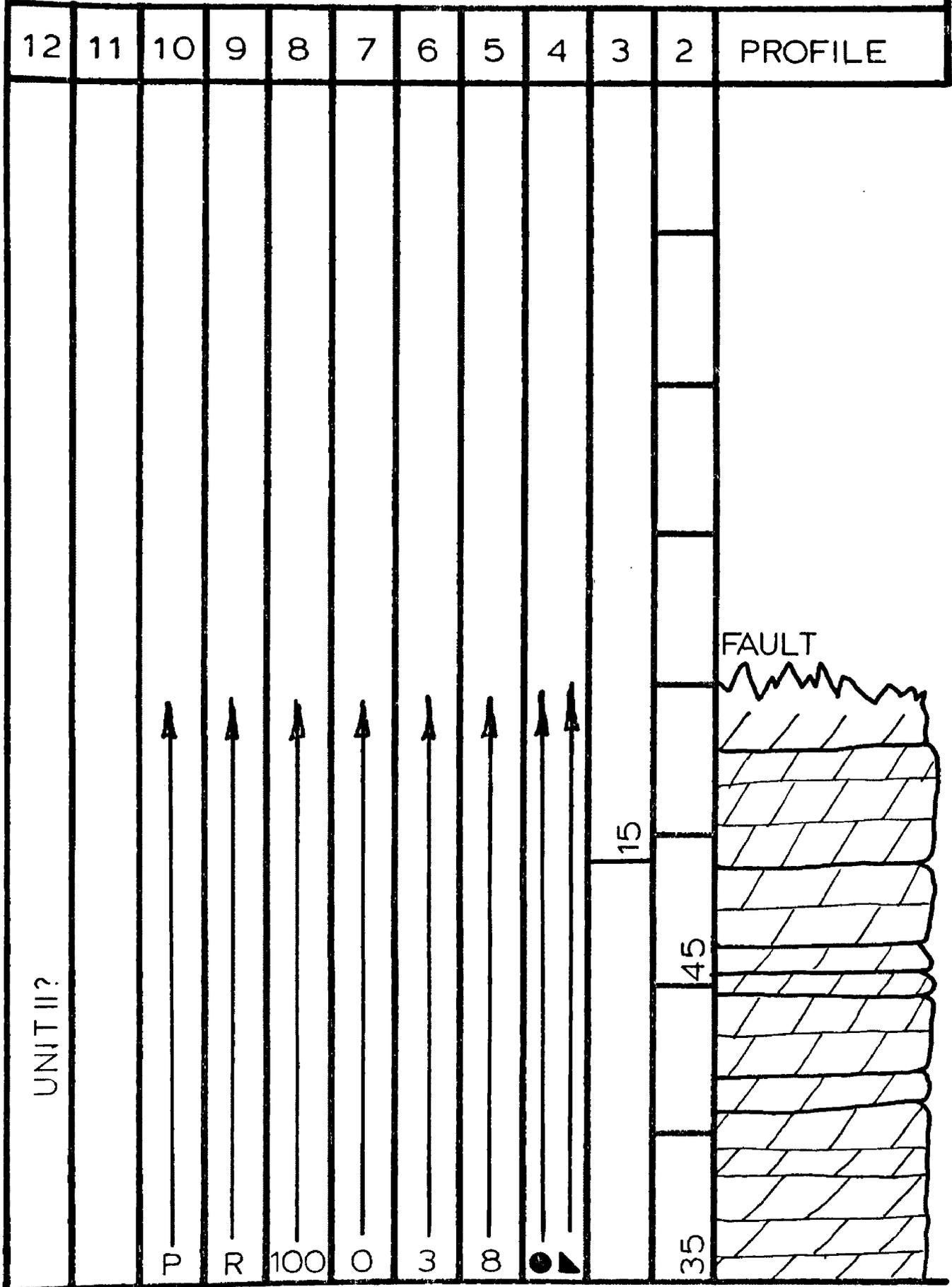
# Section 5



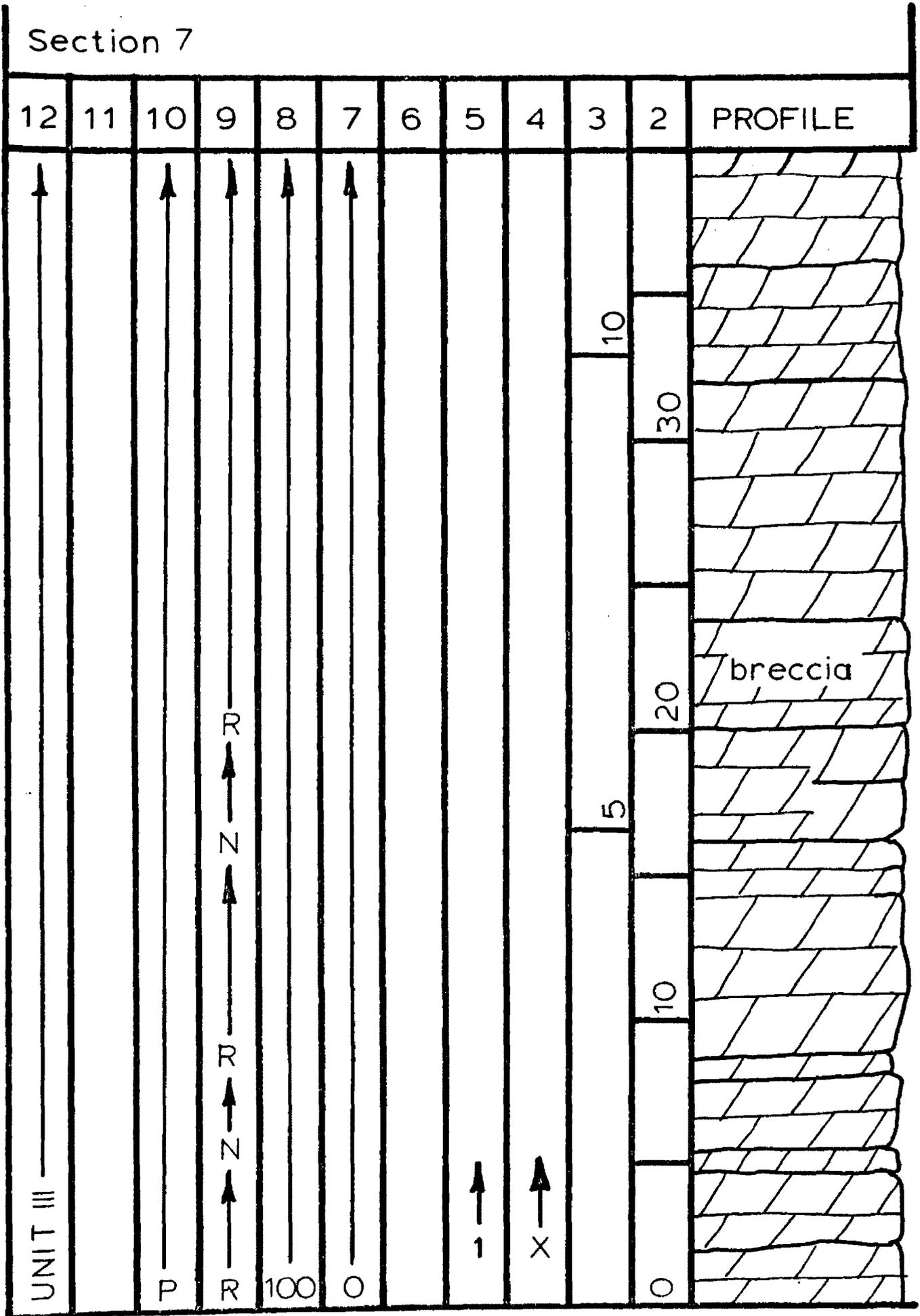
Section 6



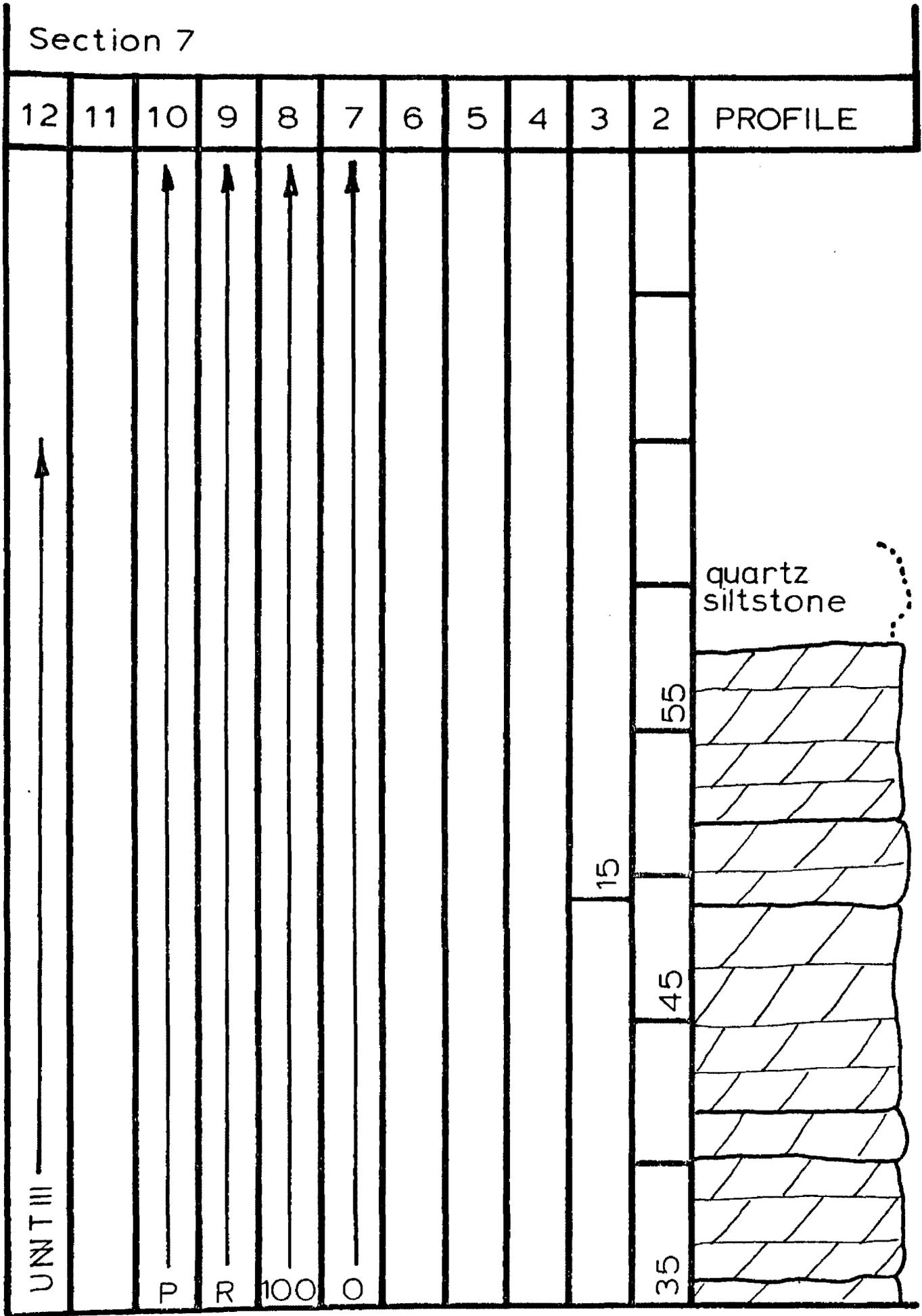
Section 6



Section 7

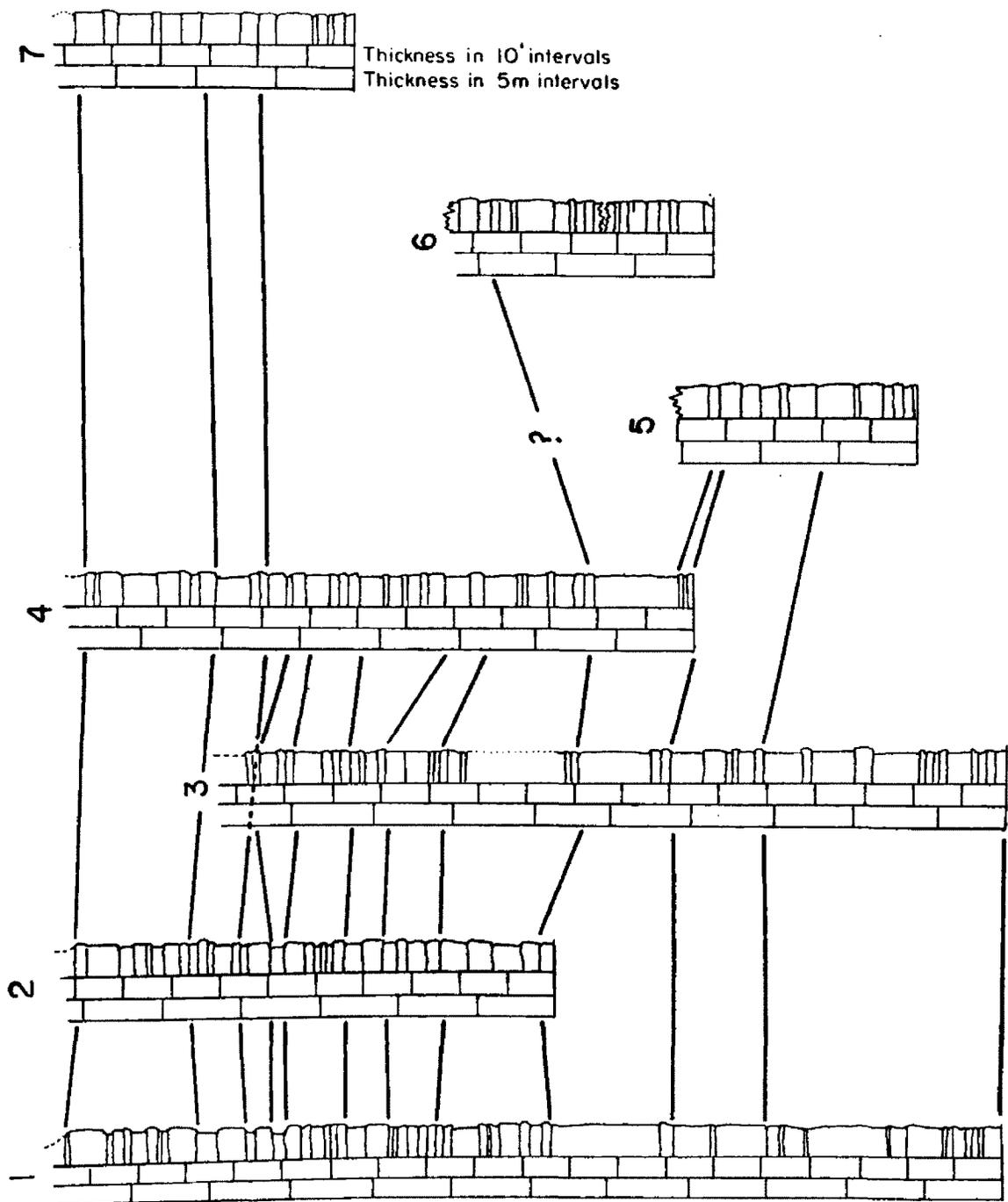


Section 7



## APPENDIX II

### Correlation of Measured Sections



APPENDIX II  
Correlation of measured sections