SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 811 AVHANDLINGAR OCH UPPSATSER ÅRSBOK 79 NR 5

JOHN T. SANFORD AND
ROBERT E. MOSHER

INSOLUBLE RESIDUES AND GEOCHEMISTRY OF SOME LLANDOVERIAN AND WENLOCKIAN ROCKS FROM GOTLAND

UPPSALA 1985

SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 811 AVHANDLINGAR OCH UPPSATSER ÅRSBOK 79 NR 5

JOHN T. SANFORD AND
ROBERT E. MOSHER

INSOLUBLE RESIDUES AND GEOCHEMISTRY OF SOME LLANDOVERIAN AND WENLOCKIAN ROCKS FROM GOTLAND

UPPSALA 1985

ISBN 91-7158-340-8
ISSN 0082-0024

IUGS
UNESCO
IGCP

Project
ECOSTRATIGRAPHY

Address:
John T. Sanford (†)
Robert E. Mosher
Dept. of Geology,
Wayne State University,
Detroit, Michigan, USA

Fotosats: ORD & FORM AB
Tryck: Offsetcenter AB, Uppsala 1985

CONTENTS

ABSTRACT

Sanford, John T., and Mosher, Robert E., 1985: Insoluble residues and geochemistry of some Llandoverian and Wenlockian rocks from Gotland. Sveriges geologiska undersökning, Ser. C. No. 811, pp. 1–31. Uppsala 1985.

This is the first of two papers, the purpose of which is to present the results of research carried out on several hundred specimens of sedimentary rocks collected on the Swedish island of Gotland. Studies included stereoscopic microscopic examination, some petrographic microscopic examination and quantitative chemical analyses of the acid-soluble fractions for CaO, MgO, FeO, and P. The insoluble residues were considered to be a separate phase with a separate history and were also analyzed quantitatively. Values are given for fine, coarse and total insolubles and these data are further broken down into clastic and nonclastic components.

The area of study in this paper covers the range of age from Late Llandovery through Wenlock time and discussions of the lithology, chemistry and mechanisms of diagenesis from the Lower Visby Beds to the Lower Mulde Beds are included.

An attempt is made to relate the chemical analyses to the modes of diagenesis, and trends in the quantitative distribution of clastic materials are illustrated. Speculations are given in an attempt to relate iron and fine clastic content of the sediments to the degree of dolomitization and comparisons are made with rocks of similar age and environment of the Michigan Basin.

INTRODUCTION

The Swedish island of Gotland, situated in the Baltic Sea, exhibits a classic Silurian section. With the exception of a few meters of Llandovery age the strata were deposited during the Wenlock and Ludlow Epochs. The Burgsvik Sandstone occurs in the Ludlow, but the remaining rocks are limestones and calcareous shales and often contain appreciable amounts of silt and clay. Bentonitic beds are present, particularly in the lower part of the section, and bioherms of varying age interrupt the regularity of the stratification throughout the column. The beds represent a shelf environment subject to mild diastrophism which resulted in slow regional migration of the littoral zone.

Interest in Gotland coincides with the development of Silurian stratigraphy and dates well back into the last century. Its stratigraphy has been summarized recently by Laufeld (1974a) and discussed by Manten (1971) who emphasized the reefs. Hede who is responsible for much of the detailed stratigraphy has published descriptions of the beds (Regnéll & Hede 1960). All of the above references are in English, as is the indispensible catalog of Gotland exposures by Laufeld (1974b). This reference gives precise descriptions of the locations, stratigraphic information and indicates the characteristics of the exposures. Each exposure has a designated code name and number (used herein) and provision has been made for maintaining a master file at Allekvia, the research center on the Island where any additional localities can be added.

The general stratigraphy to date is well known but has been based on paleontological data and general descriptions of the rocks. Very little analytical data are available. This research attempts to redefine and quantify lithologic descriptions in order to achieve more precise comparisons of the rocks. An analytical approach, while descriptive, also reduces some parameters of the lithologies to numerical values. This allows a statistical approach to interpretation and furnishes a more detailed background for correlation with the results obtained by other stratigraphic techniques.

Field work for the study was carried out in 1972. Thanks to the help of Swedish geologists, we were able to obtain a reasonably representative group of samples including at least portions of all of the principal formations. The samples range from grab samples at the smaller exposures where only a few decimeters of section are exposed to carefully collected suites of samples, spaced by means of random numbers, whenever this was feasible. These were supplemented by specimens of any unique lithologies, contact zones or other critical material. While exposures available in low terrain of this type allow only partial accessibility to the section some of the formations are well exposed in sea cliffs or quarries. These samples allow an overview of the lithostratigraphy and indicate distinct possibilities for more complete and detailed studies.

The analytical procedures, both physical and chemical, are simple but provide refinement and quantification to the basic description of the lithology. Lithological description with the aid of the stereoscopic microscope at low powers provided the basis for correlation of subsurface Palaeozoic strata when it became apparent at an early date that fossils had some limited use. This success, widely adopted in American oilfield geology, suggested that more detailed descriptions could be even more valuable and the techniques described here are an attempt to provide this information. The data are limited to fundamentals. No attempt at this time has been made to determine trace elements or details of petrographic relationships.

The general treatment of samples has been previously described (Sanford, Mosher & Friend 1968, Mosher 1972, Mosher & Sanford 1978) but will be reviewed here in terms of current practice. It is based on the obvious fact that sedimentary rocks are made up of two genetically different types of materials – clastic and nonclastic – and that these two fractions should be analyzed individually. The term clastic is used *sensu strictu* and does not include the socalled "bioclastics", of which there are many on Gotland. In this sense clastic materials are fragments derived mechanically from a rock, formed in another environment and at a different geologic time than the formation of the sedimentary rock in which they are found. Fortunately, the clastics are largely insoluble in dilute hydrochloric acid and the chemical and biochemical sediments frequently dissolve. Siliceous materials of the latter type are an exception but these are determined microscopically in the insoluble residues. Clastic carbonate fragments offer a more difficult problem but, when not recrystallized, may be recognized during the microscopic description of gross lithology. Thus stratigraphic microscopical description of the rock and estimates of the constituents of an HCl-insoluble residue and a chemical analysis of only the acid-soluble portion of the rock provide fundamental data. Whole rock chemical analyses are not used as they combine the clastic and nonclastic elements and may be misleading in genetic studies.

Detailed individual analyses and description of all specimens involved in this study are being placed on file at Allekvia and at the Geological Survey of Sweden so that they may be available to other interested workers. Specimens and detailed analyses etc., Wayne State University, Detroit, Michigan.

METHODS

Relatively small amounts of rock are required for all analyses and it is not desirable to use jaw crushers or to screen raw rock materials because of the certainty of contamination with small amounts of copper, zinc, iron, and possibly other elements. Preferably, one collects fresh flakes of rock in the field and cuts off the required amount in the laboratory using tile "nippers" with hardened steel blades. This reduces risks of gross contamination. Sample size can be adjusted for extremely large or small quantities of residues as estimated by microscopic description. To determine the insoluble residue, five grams of rock are weighed and dissolved in one and one half times the amount of dilute HCl theoretically necessary to give complete solution using tallform beakers. Allow to stand until the solution is clear, usually 12 to 24 hours. Remove supernatent liquid by suction and apply the barium test for sulfate. Add water, allow to clear and remove by suction. This is repeated several times to remove the acid. A deflocculant is added to the final wash water. The sample is then wet-sieved using a sieve with 0.05 mm openings separating the insolubles into "coarse" and "fine" fractions, silt and clay as well as finest nonclastics. The coarse fraction is transferred to a weighed 50 ml beaker and the fines are filtered off. Both are dried and weighed before microscopic examination and description. Estimates are made of the amounts of clastic and nonclastic materials in each fraction and additional estimates may be made of any critical materials present. Consistent results indicate reliability.

Two hundred-milligram samples are preferred for chemical analysis, but when necessary, samples of 50 to 100 milligrams can be used with good results. Expert technique and accurate analytical balances are essential.

For chemical analysis the weighed sample of rock is dissolved in 1.0 Normal hydrochloric acid and the solution diluted to a known volume using volumetric glassware. Accurately measured aliquot portions of the filtered supernatent solution are then taken for chemical analysis. Quantitative analysis of these aliquots is performed for the various constituents.

Calcium oxide and magnesium oxide are determined by titration with ethylenediamine tetraacetic acid (EDTA). Iron determination is based on the quantitative color reaction with orthophenanthroline and phosphorus determination on a quantitative heteropoly-blue color reaction. A qualitative test for sulfate is made, and carbon dioxide content and insoluble residue are calculated from the total oxide content. Determinations of lead, strontium, nickel, aluminum, copper, and zinc should be included if proper equipment is available.

These methods are modifications of recognized analytical procedures and have been designed for the simultaneous handling of large numbers of samples in any laboratory having simple equipment and instruments. Manual manipulation has been reduced to a minimum. The methods are compatible with automation and computerization with direct read-out.

Accuracy is excellent. The analyses for calcium oxide and magnesium oxide have an error of less than 10 parts in a thousand. Error in iron analysis is less than 30 parts in a thousand as indicated by duplicate analysis of the same samples by these methods and by atomic absorption analysis (Lilienthal 1972).

Bureau of Standards-Analyzed samples of dolomite and limestone have been used to verify the accuracy of our procedures.

1.0 Normal hydrochloric acid is preferred as solvent for sedimentary rocks since it minimized leaching of metals from silicate minerals and clays, which are often present, and is compatible with standard methods for making insoluble residues.

The qualitative test for sulfate is necessary since the presence of large amounts of gypsum or anhydrite affects subsequent calculations and interpretation.

Discrepancies introduced through the use of two separate samples are usually not great as most sedimentary rocks are remarkably uniform in composition and uniformity can be checked with the stereoscopic microscope prior to analysis.

Lack of success with the use of insoluble residues and their diminishing popularity has resulted from dependence on qualitative methods and the common practice of discarding the finer residues during the washing procedure. As a result only conspicuous differences in the coarser fractions have been noted. Consequently, stratigraphic correlation was usually limited to the tracing of those horizons which contained qualitatively unique insolubles. When quantitative values for both soluble and insoluble portions of the rock are available there is a probability that characteristic patterns will develop which can be compared and correlated. Trends within formations may be identified so that groups of beds as well as individual lithologies are useful in correlation and interpretation. This is demonstrated later in the discussion of the various stratigraphic units.

However, in establishing trends as well as in determining what may be considered atypical beds, emphasis has been placed on those well-stratified beds which probably have not been strongly influenced by bentonitic materials. Bentonitic lithologies as well as those of reef masses have been more strongly influenced by the immediate special conditions of sedimentation than by the influence of an evolving set of paleographic conditions. Their characteristics have been controlled by one critical factor and the minor but important differences resulting from regional factors which might suggest stratigraphic positions have been modified or masked.

Both bentonitic and biohermal lithologies appear to have common characteristics throughout the section rather than differences. These cannot be neglected but must be fitted into the interpretation dictated by the more normal deposits. The means of the data are presented in Table 1 to which reference should be made regarding the various beds.

TABLE 1. Summary of analytical data. Visby Beds to Mulde Beds.

FORMATION	LOCATION	INSOLUBLES % C	% NC	% Sol	% CaO	% MgO	% FeO	% P	No. SAMPLES	INTERVAL	REMARKS
MULDE											
Lower Part	Blåhäll 1	62.4	Tr	37.6	11.28	3.14	1.27	0.031	3	2.00 m	Siltstones interbedded
		30.1	Tr	69.9	33.80	2.02	0.79	0.022	4		Limestones
HALLA											
Bara Oolite	Bara 1	2.2	0.2	97.6	52.77	1.24	0.25	0.011	3	These sections not measured but involve only a few meters	
SLITE											
Reef, Slite	Bara 1	5.7	0.1	94.3	51.95	0.74	0.31	0.011	3		
Siltstone	Mulde 1	18.1	–	82.0	38.42	5.69	1.66	0.083	1	No M	
Siltstone	Svarvare 1	24.6	–	75.4	35.10	4.74	0.20	0.46	1	No M	
P. gotlandicus Beds?	Svarvare 1	–	39.9	60.2	24.03	3.37	1.29	0.054	1	No M	
Lms Quarry, unit g	Slitebrottet 1	0.9	0.1	99.0	54.80	0.53	0.11	0.009	4	2.65 m	
Unit Upper zn?	Slitebrottet 1	5.9	0.2	92.9	51.21	1.21	0.56	0.007	18	21.00–34.18 m.	Bentonitic horiz., excluded
Transition	Slitebrottet 1	9.6	0.1	91.5	48.84	1.48	0.50	0.007	8	15.00–21.00 m.	No bentonite in section
Lower Zone	Slitebrottet 1	14.4	0.1	85.0	45.21	2.00	0.83	0.007	24	0–15.00 m.	2 bentonitic samples excluded
TOFTA											
Lower Part	Galgberget 1	2.0	Tr	98.0	54.13	0.63	0.08	0.004	6	2.95 m	
Unconformity zone	Galgberget 1	21.6	–	78.5	45.05	1.11	0.26	0.012	2		
HÖGKLINT											
Undiff. Upper Mid.	Galgberget 1	1.7	0.2	98.1	54.70	0.49	0.05	0.007	5	2.00 m	
Bioherm	Ireviken 3	1.0	0.1	98.9	54.69	0.50	0.07	0.004	6	Grab	
Unit a?	Ireviken 3	24.1	0.5	75.4	35.70	2.65	1.61	0.013	7	5.1 m	
VISBY											
Upper	[1]Ireviken 3	Note, separated on lithology – stratigraphy irrelevant									
Upper	[1]Gnisvärd 1	21.6	0.2	78.3	40.35	1.41	0.47	0.013	1	Loose	
Lower	Ireviken 3	Note, separated on lithology – stratigraphy irrelevant									
Lower	Nyhamn 1	44.0	0.6	55.3	21.46	2.52	1.02	0.008	Chem. 4 Res. 3	Approxm. 2 m	
[1]Total Visby exposed Ireviken 3 separated by facies											
Arg. facies		56.9	0.9	41.8	14.67	4.50	2.26	0.008	8	10.1 m	
Cal. facies		24.7	0.7	74.0	39.05	2.04	0.75	0.010	5	10.1 m	

THE VISBY AND LOWER HÖGKLINT BEDS

The Visby Beds are the oldest strata exposed on Gotland and have been placed in the late Llandovery by Hede (1960:31–52). The section shown by Gray *et al.* (1974) retains the Lower Visby in the Llandovery but places the Upper Visby in the Wenlock. The summary by Laufeld (1974a) indicates that sedimentation was continuous between the two sets of beds and that the faunal boundary is problematical. It appears that designation of precise boundaries might result in an artificial situation, although we have indicated a most probable horizon for the Visby-Högklint boundary.

IREVIKEN 3 – The section sampled at Ireviken 3 occurs in a steep sea cliff and includes beds ranging in age from Lower Visby into stratified and biohermal Högklint rocks. Complete sampling was impossible due to the character of the exposure. The data are summarized in Table 2 which indicates the averages of various parameters of the four facies present and differs somewhat from Table 1. While the arrangement is based on facies groups it has stratigraphic as well as genetic significance.

Based on the premise that rocks containing over 50% of clastic materials can be considered clastics and those with less than 50% non-clastics, the 15.2 m of the Ireviken 3 section contains a partially interbedded clastic and a non-clastic facies. No non-clastic rocks were found below 4.5 meters and no clastic rocks above 10.1 meters. The beds between these two levels contain both facies (Fig. 1). A comparison of additional parameters of the two facies as separated by clastic content indicates the validity of this approach (Fig. 2). Both facies contain a reasonably high percentage of clastics, an average of 56.8%, if the bentonites are not included, for the clastics and 24.6% for the non-clastics. The percentages for the non-clastics range from 15% to 42% with only two samples containing more than 30%. The percentages for the clastic rocks range from 50.2% to 61.3% clastics. A bentonite at 5 m contained 89.6% of clastics and one at 7.35 m, 82.0%. These beds could not be expected to follow the normal pattern as sedimentation was influenced by factors atypical to the trend in environmental evolution and peripheral to the immediate milieu. The two typical facies follow definite trends which are approximately parallel, as shown in Fig. 1.

The clastic materials in all samples are predominantly argillaceous silts, as are the clastic materials in the recognizable bentonite beds. It seems probable that the clastic fractions of both clastic and non-clastic rocks may be directly or indirectly influenced by volcanic activity. This suggests that volcanism may have been responsible for the deposition of the more clastic phases of the section and that normal agents of transportation may have introduced fine pyroclastics during lulls in volcanism. It appears that the volcanism occurred

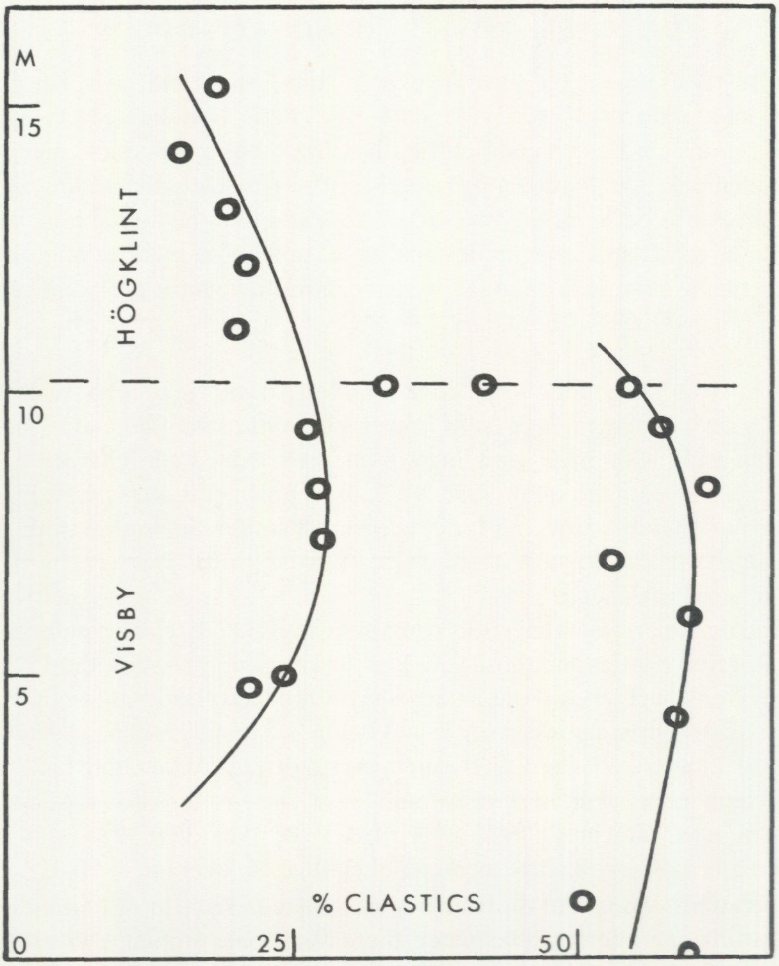

Fig. 1. Trend curves of clastic components at Ireviken 3.

outside the area of provenance as only fine materials are involved. It is not possible to make a realistic appraisal of the overall significance of pyroclastics in the Visby Beds but they must have been important.

Non-clastic insolubles are present in small amounts, commonly under 1%. Secondary silica is always present although usually not in the form of silicified fossils. Pyrite occurs in most samples as do small fragments of chitin. Scolecodonts occur at Ireviken 3 more commonly in the clastic facies, and other small fossils are found sparingly.

The insoluble fractions of a few of the specimens from this locality were examined with the petrographic microscope. Mulls of the insoluble residues were made using various oils of known refractive index and tentative

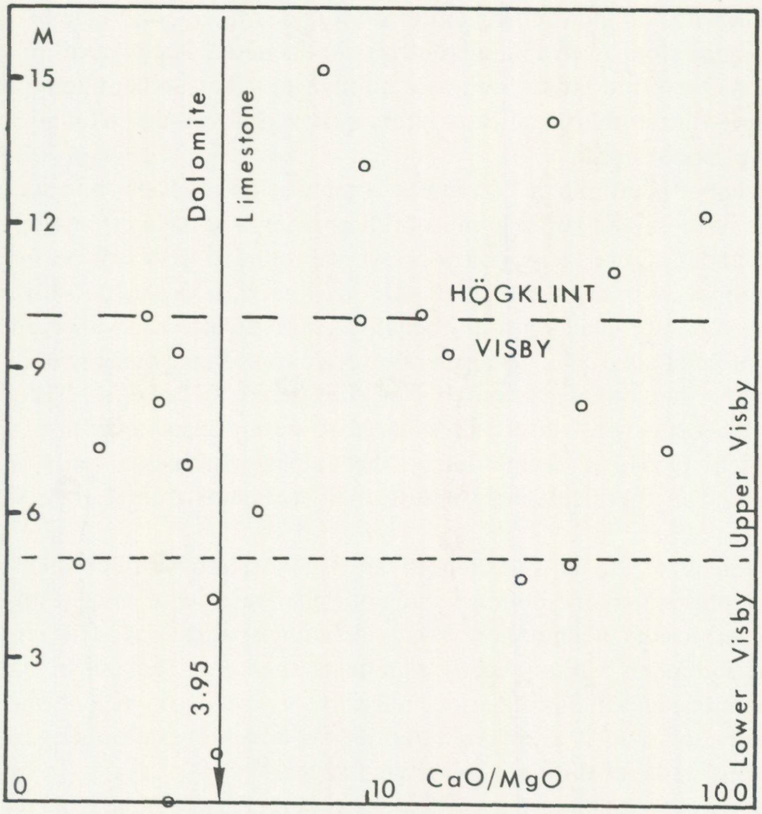

Fig. 2. Variations in CaO/MgO with stratigraphic position at Ireviken 3.

identifications of some of the minerals were made. Since most particles were less than 20 micrometers in diameter, there were some problems with identification by this means on this preliminary examination.

The residue of the specimen at the base of the exposure consisted primarily of silt with small quartz flakes and the rare small particle of feldspar. The presence of silt size grains of tourmaline seemed characteristic although the rare grain of tourmaline may be found in a number of other formations. The number and size of these tourmalines in this particular stratum would, if confirmed by others, have the potential of being an excellent stratigraphic marker.

The residue of a specimen taken from the top of the section in the non-reefal Högklint Beds contains much extremely fine silt, some small quartz grains and the occasional very small feldspar grain. An occasional minute grain of tourmaline was also seen.

The lower bentonite, at the 5 m level, was examined in the same manner. The insoluble portion was composed of clumped clay and very fine silt size particles with common subangular to subrounded fragments of albite of sand size ranging from 75 to 150 micrometers in diameter. Small grains of quartz and mica were present as well as a number of other unidentified minerals including various feldspars. Rare larger quartz grains could be found but not larger plates of mica.

The upper bentonite at 7.35 m was composed of much clay and silt, many clumps of these and larger grains of other minerals, ranging from angular to well-rounded. Very large yellow-brown subrounded plates of biotite were common, occasional grains of fine sand size quartz, feldspar (possibly albite) and the very rare small uniaxially negative grain of a material with a refractive index of less than 1.540. The general overall appearance of these grains was similar to that of quartz and it was considered to be alpha-cristobalite. Although beta-cristobalite is considered to be an unstable form of quartz (Heinrich 1965), it seems likely that alpha-cristobalite could survive unchanged in these relatively undisturbed sediments from Lower Silurian times.

A number of the above minerals can be associated with bentonite and a more sophisticated and detailed study of this nature could conceivably yield significant results in a number of ways including applications in the stratigraphy of sediments without many significant markers. The use of mulls of insoluble residues in oils of various refractive indices is convenient since they are easily and quickly prepared and offer the possibility of a wide variety of mounting media of different refractive indices.

The purity of the limestones in the Högklint reef has resulted from the local and unique conditions under which they were formed rather than to the stratigraphy even though they are considered to be younger than the Visby Beds. The small percentage of clastics (1%, see Table 1) has resulted from relatively rapid growth by accretion of biochemical carbonate above the general level of the floor where the usual relationships between the clastic and non-clastic elements in the milieu of sedimentation existed. It is also possible, although not essential to their formation, that the bioherms accumulated during lulls in the influx of clastic materials. The chemical data from the biohermal rocks are included in Table 1 and require no special comment beyond noting that they are rather pure limestones. The compositions of the soluble fractions of the various facies emphasize the differences already suggested.

It is probable that normal carbonate deposition took place at a fairly uniform rate and that the influx of clastics varied. It follows that fluctuations in the amounts of minor elements in the solubles can be compared with variations in the amounts of clastics in the rocks.

The clastic rocks represent one of the few dolomitic facies on Gotland with nine samples, including the bentonites, having a CaO/MgO ratio below 3.95, the point at which rocks become 50% dolomite (Fig. 2). In contrast, the samples from the non-clastic facies are magnesian limestones. The Table indicates an average ratio of 16 and the twelve ratios range from approximately 7.8 to 33.

As the Visby sediments contained fine and apparently impervious muds there was reduced opportunity for circulation of sea water below the interface, so dolomitization must have been syngenetic and not early diagenetic as was the situation with many of the extensive dolomites in the Niagaran of Michigan and Ontario. There is a definite correlation between the incidence of dolomitization and the higher clastic percentages at Ireviken 3 and the two must be related. Before this relationship is considered further, some reference should be made to the distribution of iron in the Ireviken 3 sediments. Reference to Table 1 shows a much higher percentage of iron in the clastic than in the non-clastic beds. The non-clastic rocks average 0.75% FeO and the clastic rocks 2.26% FeO. The relationship is clear; clastics, dolomite and easily soluble iron content are related.

Vinogradov (1953, p. 575) has indicated that iron and other heavy metals tend to accumulate in silt or silty water. The correlation between the occurrence of FeO and clastic content is even more striking when it is considered that the relatively clastic-free biohermal Högklint rocks average only 0.07% in the six samples and the two bentonites with an average of 85.8% clastics have an average of 0.06% FeO in the samples although the total solubles average only 14.2%. This suggestion is further developed in the discussion of the Slite Beds.

The question is raised as to whether the presence of iron is the cause of or the result of dolomitization. Apparently, the presence of the Fe^{++} ion is an essential to the formation of dolomite, either syngenetically or diagenetically. It acts as a catalyst as its ionic radius is intermediate between that of Ca^{++} and Mg^{++} (ionic radii of Ca, Fe and Mg are 0.99, 0.75 and 0.65 ångstroms, respectively). The calcium ion in calcium carbonate is first replaced by ferrous ion which is in turn replaced by magnesium ion. This sequence is more readily accomplished than the direct replacement of Ca ion by Mg ion. The process usually leaves some residual ferrous iron within the dolomite.

The dolomite siltstones of the Visby Beds have much more associated iron than pure dolomites. A nearly pure dolomite from the Engadine Formation of Chippewa County, Michigan, has the following composition as shown by an average of nine determinations: CaO 30.38%, MgO 21.55% and FeO 0.0164%. The CaO/MgO ratio is 1.4 and only traces of insolubles are present. A section of the Engadine Formation 245' thick (74.7 m) from the subsurface of Beaver Island in Lake Huron has also been analyzed. It was a reasonably pure dolomite with a CaO/MgO ratio of 1.4 and an average FeO content of 0.0346%. The calculated insoluble content of 2.5% is mostly non-clastics.

These are diagenetic dolomites and there must have been free circulation of sea water below the interface during the process of dolomitization to provide magnesium and allow the excess calcium and iron to be flushed out.

The Visby muds, as previously stated, were impervious. The carbonate was formed syngenetically, as there was an abundance of catalytic iron attracted by the presence of the fine clastics possibly as a surface effect. The excess iron was not washed out and remained in the sediment. This situation can be found elsewhere. It could also explain incomplete dolomitization. Reference to the Beaver Island section, mentioned above, shows an average of 0.237% of FeO in 70 feet (21.3 m) of a section analyzed from the Alexandrian (Llandoverian). The section contains both a higher content of FeO and a higher percentage of insolubles (average 10.2%) than associated Silurian formations. The insolubles are composed of silt, clay and gypsum. A similar relationship exists with respect to subsurface Alexandrian rocks from Grand Traverse County, Michigan, as clastics increase FeO increases.

The relationship between fine clastics and the precipitation of iron probably results from the relatively high chemical energy associated with the large surface areas available from very small particles in fine grained deposits. This usage of the term energy is in contradistinction to the use of "high energy" when referring to environments of high mechanical energy.

As shown in Table 2 the percentages of phosphorus also tend to increase as the percentages of clastics increase. The average value for the percent of phosphorus in the clastic facies is the one exception to this but the correlation is unmistakable. As in the case of iron there is also a stratigraphic progression as the bentonites are interbedded with the clastics in the lower part of the section. The non-clastics overlap the clastics but start higher and continue higher in the section. The biohermal rocks with the least phosphorus are at the top. If the assumption that normal carbonates at this locality formed at about the same rate is correct, then the percentages of solubles would be a rough index as to the relative rates of formation and the influx of clastics would take place during the time interval indicated by the amount of carbonate at any particular horizon. It seems probable that the bentonitic beds formed more rapidly than any of the other facies. The occurrence of phosphorus in the bentonites is high but it is also erratic, 0.0159% for the lower at 5 m and 0.2077% for the upper at 7.35 m. The higher phosphorus values in the bentonites are best explained by rapid overkill on an organically productive sea bottom with little opportunity for subsequent removal of phosphorus. It is not necessary, however, to provide a particular source for the phosphorus as there is a sufficient amount in normal sea water, assuming that, as seems probable, Silurian seas were not vastly different from those of today (Vinogradov 1953, p. 569).

The same assumption applies to many other elements. It is only necessary to provide an adequate modus operandi for withdrawal and precipitation to

TABLE 2. Summary of means, by facies.

	Solubility		Insoluble					
FACIES	[1]Calc.	[2]Res.	% C	% NC	CaO %	MgO %	FeO %	P %
Ireviken 3								
Biohermal	98.6	98.9	1.0	0.1	54.69	0.50	0.07	0.004
Non-clastics	73.3	74.8	24.6	0.6	37.10	2.39	1.25	0.012
Clastics	39.5	41.8	56.8	1.5	14.68	4.50	2.21	0.008
Bentonitic	7.4	14.2	85.8	0.0	2.10	1.21	0.60	0.112
Nyhamn 1								
	45.6	47.7	51.6	0.7	21.47	2.52	1.11	0.008

FACIES	CaO/MgO	MgO/FeO	No. Samples
Ireviken 3			
Biohermal	118	12	6
Non-clastics	16	2.3	12
Clastics	4.1	2.1	
Bentonitic	1.7	2.0	2
Nyhamn 1			
	9.3	2.4	4

[1]Calc. = calculated, chem. anal.
Res. = from residue analysis

explain the deposits. The most obvious agency for precipitation of phosphorus compounds is the activity of various organisms, not necessarily as shell or other tangible lithological material but within body tissues which could accumulate within the sediments and later disappear. The potential of normal seawater as a source of phosphorus has been suggested by Seiwell and Sanford (Seiwell 1935), who estimated that a Silurian horizon two to three centimeters thick and extending over a circular area of 13.7 km could contain 75×10^7 kilograms of phosphorus. Subsequent work has shown that this horizon, while not everywhere equally rich in phosphorus has a much greater extent than the area originally postulated.

Assuming that the phosphorus in the Ireviken 3 section is the result of organic precipitation from normal Silurian seawater it appears that lower phosphorus accumulation in the reef rocks resulted from the fact that removal of organic material must have been more rapid in the bioherms than in the less permeable deposits.

On the basis of lithostratigraphy, there seems to be little reason to divide the Visby into lower and upper members or to separate the bedded (ribbon) limestones opposite the lower portion of the biohermal mass from the Visby as Lower Högklint. Although there may be some biostratigraphic data suggesting these subdivisions, the physical and chemical environmental controls responsible for the character of the sedimentation appear to have undergone an orderly and natural progression from a preponderantly argillaceous to a calcareous facies. It is probable that sedimentation was continuous and that there was a relatively brief transitional phase between Visby and Högklint time. Differences in the fossils may be explained by environmental control of the fossil communities as well as by stratigraphic succession.

GNISVÄRD 1 – A single sample of material excavated from the harbour at Gnisvärd and a loose weathered carbonate represent a limestone from the Upper Visby Beds. The loose carbonate sample is a medium grey, very fine to finely crystalline fossiliferous limestone. The insolubles consist of 21.6% of argillaceous silt and 0.2% of secondary silica and weathered sulfides which partly represent fossil forms. The solubles represent a fairly pure limestone with a CaO/MgO ratio of 29, 0.47% of FeO and 0.013% of phosphorus. Solubility of the iron salts may have been increased by weathering.

NYHAMN 1 – The Lower Visby Beds were also sampled at Nyhamn 1 where approximately two meters of section are exposed. As at Ireviken 3, the clastic materials are composed of silt and clay although the clay content is higher. The clastics decrease upward and average 51.6% in spite of a low figure of 17.4% for the top sample. The chemistry of the solubles at Nyhamn 1 is not greatly different from that of the clastic facies at Ireviken 3. As these rocks are similar in both age and facies this requires no special comment.

HÖGKLINT-TOFTA CONTACT

GALGBERGET 1 – The small quarry at Galgberget 1 provides evidence of mild Silurian tectonism in the form of an angular unconformity between the Högklint and Tofta Beds. This quarry exposes 2 meters of the Högklint Beds and 2.95 meters of the Tofta Beds.

The Tofta Beds rest on the Högklint Beds at an angle of approximately 3 1/2° and the latter dip easterly approximately 6° indicating that gentle movement occurred both before and after Tofta time. The characteristics of the beds make precise measurements difficult. Unlikely as this structural situation may appear in an area with locally imperceptible regional dip, more striking evidence of an unconformity is present in the lithologic characteristics of the rocks. Descriptions of the general characteristics of the lithologies and the fossils will be found in Hede (1960, p. 55–56).

The Högklint Beds are limestones which contain limestone fragments ranging from coarse sand to rounded pebbles up to 10 to 15 mm in diameter. The matrix is medium to coarsely crystalline calcite and there is some greenish argillaceous interstitial material (possibly celadonite or a similar substance).

The upper Högklint Beds are crinoidal. The pebbles resemble wave-worked rounded pellets of calcareous material similar to some currently being formed by wave action on an Hawaiian beach. The pebbles and sand-size fragments are certainly not truly clastic but represent reworking of material formed contemporaneously within the Högklint environment. Hede (op. cit.) mentions that the "limestone is in part conglomeratic". The gross lithology suggests shoaling and a littoral milieu attendant on events responsible for the angular unconformity. The Högklint Beds average 1.7% of true clastics with range of from 1.0% to 2.5%. These clastics are silty clays with a few sand grains in the lower part. The non-clastic insolubles include silica and a little weathered sulfide.

The light grey shaly-appearing material along the unconformity has been included in the Högklint Beds by Hede (op. cit.) and in the Tofta Beds by Laufeld (oral communication). As it appears to be a lag deposit, probably reworked during early Tofta time, we agree with Laufeld's interpretation. Hede describes this zone as marly and conglomeratic with an "uneven and ill-defined" lower limit "whereas the upper limit is usually even and sharp". The rock along the unconformity is in reality a limestone with a solubility of 78.5% and a CaO content of 45.05%. It has the gross appearance of a light grey clay containing limestone fragments and Hede (op. cit.) reports a variety of "fragmentary and strongly worn" fossils. Examination of the acid-insoluble residue of this "lag" deposit with the petrographic microscope indicated that approximately 10% of the sand-size material consisted of subangular to subrounded grains of orthoclase feldspar along with very fine to medium grained angular to subangular quartz and quartz/orthoclase. The presence of feldspar was confirmed by x-ray diffraction analysis. A few grains are up to 0.7 mm in size. This is the most striking feature of this contact zone. It is certainly evidence for the "lag" characteristics of this accumulation which we term a "microlag" deposit, as the granite wash constituents are present in such small amounts and so stratigraphically localized.

The material at the contact zone varies significantly from the two sets of beds in its chemical characteristics. It has a CaO/MgO ratio of 41, 0.264% FeO and 0.012% P. These higher MgO, FeO and P values as compared to both Tofta and Högklint Beds may be due in part to the presence of relatively greenish-grey silty clay but they may also reflect the greater time span allowed for chemical and biochemical precipitation during the time lapse indicated by the unconformity. The presence of traces of glauconite strengthens this interpretation as it may indicate a slow rate of sedimentation.

The Tofta Beds are predominantly light-brown, finely crystalline to dense limestone although they are variably crystalline at the base and there are some occurrences of medium-sized crystals. Also near the base there are a few patches of greenish clay. Fossils are for the most part fragmentary or indistinct, although there are some ostracodes; "*Leperditia*" among other fossils is reported by Hede (1960). The percentages of clastics in the Tofta Beds, excluding the argillaceous zone, averaged 2.0% and range from 0.5 to 2.6% for six samples with the lower percentages being at the top and bottom of the Tofta section. The body of the formation consistently contains 2.4% of clastics. Clays predominate in the insolubles although silts are present. Non-clastic insolubles are negligible although sulfides are present throughout the section. In the bottom sample immediately above the contact zone there is an abundance of small to very small pellets of pyrite. This pyrite may reflect the presence of the unconformity and a break in the rate of sedimentation. The mean CaO/MgO ratio of 95 indicates a pure limestone. The percentage of FeO is only 0.08% and there is also a low percentage of phosphorus, 0.004%. The general appearance indicates less mechanical energy and possibly somewhat deeper water during Tofta than during Högklint time.

The analytical results do not indicate any great differences between the Högklint and Tofta Beds. Except near the contact zone non-clastics occur only in traces in the residues and consist primarily of sulfides although there is a little white siliceous material in the Högklint Beds. The clastics are fine consisting primarily of silty grey clay in both rocks although there is a little brownish and greenish clay in the Tofta Beds. Clastic levels are similar. The CaO/MgO ratios average 95 for the Tofta and 120 for the Högklint rocks. On the average FeO is present in slightly greater amounts in the Tofta Beds, 0.088% as compared to 0.048% in the Högklint Beds. Phosphorus is greater in the Högklint (average 0.007%) than in the Tofta (average 0.004%). The differences do not appear to have any marked significance.

The low-angle nonconformity at locality Galgberget 1 shows evidence of mild tectonism. Both the physical and chemical characteristics of the sediment at the contact are perhaps more striking than the low angularity. This mild tectonism did not change the general paleogeography of the area to any great extent.

Although the tectonic events at this locality are somewhat unusual in terms of Gotland stratigraphic history, the evolutionary trend of the regional environment did not change as shown by the similarities between the Högklint and Tofta Beds.

THE SLITE BEDS

These beds consist of a sequence of interbedded argillaceous limestones and calcareous shales with several beds which might be properly classed as impure bentonites. There are also massively bedded and biohermal rocks. The most complete exposure sampled was Slitebrottet 1.

A few samples were collected from several other small exposures where there was too little section to warrant detailed sampling. These are of interest primarily for comparison with the samples from Slitebrottet 1 and to demonstrate the general character of the Slite Beds.

SLITEBROTTET 1 – The Slite Beds are particularly well exposed in the large cement company quarry at Slite where we measured slightly more than 34 meters of interbedded limestones and shales ("marls") with a number of distinctive bentonite beds. The beds at this locality were initially described by Hede (1960) who placed them in the Slite Group.

Manten (1971, p. 317) discussed the "Slite Marlstone" of the Slite area and gave ranges of composition for a number of minerals including calcite, dolomite, quartz, feldspars, mica, illite, and kaolinite with traces of iron compounds. No methodological details were given.

Further description has been made by Laufeld (1974a, pp. 121–122) who refers to them as Slite Marl. In the same reference (p. 167), the sections at both Slitebrottet 1 and 2 are listed as "Slite Marl, undifferentiated". In his discussion of the Chitinozoa (also 1974a, p. 33) Laufeld indicates that at Slitebrottet 1 the Slite Marl is overlain by "unit g". We are uncertain as to the exact location of this boundary.

At this locality we measured a total of slightly more than 34 meters of beds and collected 53 representative specimens ranging from the quarry base (Reference Level "0") to the top of the exposure (34.18 m) at measured intervals, which were established by means of random numbers. Both the argillaceous limestones and shales or "marls" were included and in addition several beds categorized as bentonites were sampled. These were located at 0 + 1.75 m, 0 + 3.75 m, 0 + 10.00 m, and 0 + 23 m. All of these specimens were analyzed by the methods previously described (Mosher & Sanford 1978) for insoluble residues and chemical composition. In addition, a few of the insoluble residues have been studied with the petrographic microscope.

The results of both chemical and residue analyses suggest that the strata exposed at Slitebrottet 1 should be divided into upper and lower subdivisions with a transitional zone separating them. This transitional zone is approximately six meters thick and as is frequently the case in similar situations might be given different limits by other workers. Some might wish to place a more definite boundary between the upper and lower beds.

Variations in the percent of clastics are the most obvious indicators of the subdivision . The clastics as they appear in the insoluble residues are argillaceous silts and silts with occasionally small amounts of fine sands. They do not differ greatly in overall character throughout the section but the amounts vary considerably, being greater and having a greater range in values in the lower than in the upper part of the section. The data are summarized as mean values

TABLE 3. Slite section at Slitebrottet 1.

Divisions	Interval	$\bar{X}$ % C	Range % C	$\bar{X}$ CaO/MgO	Range CaO/MgO	No. of samples
Upper Beds	21–34 m	5.9	1.7–14.8	46	24–80	18
Transition Zone	15–21 m	9.6	4.4–12.3	36	23–64	8
Lower Beds	0–15 m	14.4	3.6–28.4	28	8–95	24

in Table 3. The bentonite beds have not been included in calculations of these data. Note the intermediate value and the lower range of %C in the transitional zone. The differences between the Lower and Upper beds indicate a marked shift in conditions in the overall environment during the deposition of the transition beds.

Clastic trend curves can be sketched for the upper and lower parts of the section and it is possible to extend the curves for both beds into the transition zone with a certain amount of overlap possibly indicating alternating environmental trends during deposition of the latter beds (Fig. 3). This figure should be compared with Fig. 1 (Ireviken 3) which demonstrates parallel development of two facies in the Visby Beds. While there is some scatter (range in values) among the plotted points the normal trends are well developed and definitive. The distribution of the percentage points for the lower beds suggests the probability that a secondary (lower clastic) environmental trend existed during the early part of that deposition and that beds compatible with this trend were sometimes deposited.

The character of the carbonates, as shown by the calcium oxide to magnesium oxide ratios adds strength to the stratigraphic interpretation suggested above. Reference to Table 3 indicates an upward increase in these values and a greater range in the Lower than in the Upper beds. The transition zone has the lowest range and as indicated by the data from the clastics its limits may be subject to varying interpretations.

Disregarding strata with clastics in amounts of 40% or 50% which we assume to have been influenced by tephra, probably wind blown, and the high percentages in adjacent beds there are other strata throughout the entire section with more clastics than would appear to be indicated by the general environmental trends. Could these have resulted from lesser volcanic activity or contain tephra reworked from nearby deposits? Until these silts and clays are studied in more detail this must be a moot question. The degree to which tephra have influenced the sediments throughout the section cannot be determined by our technology but the data suggest that it may have been an important one.

The non-clastic insolubles appear to be too small in amount to have any stratigraphic importance. It is noteworthy that not only is the mean value

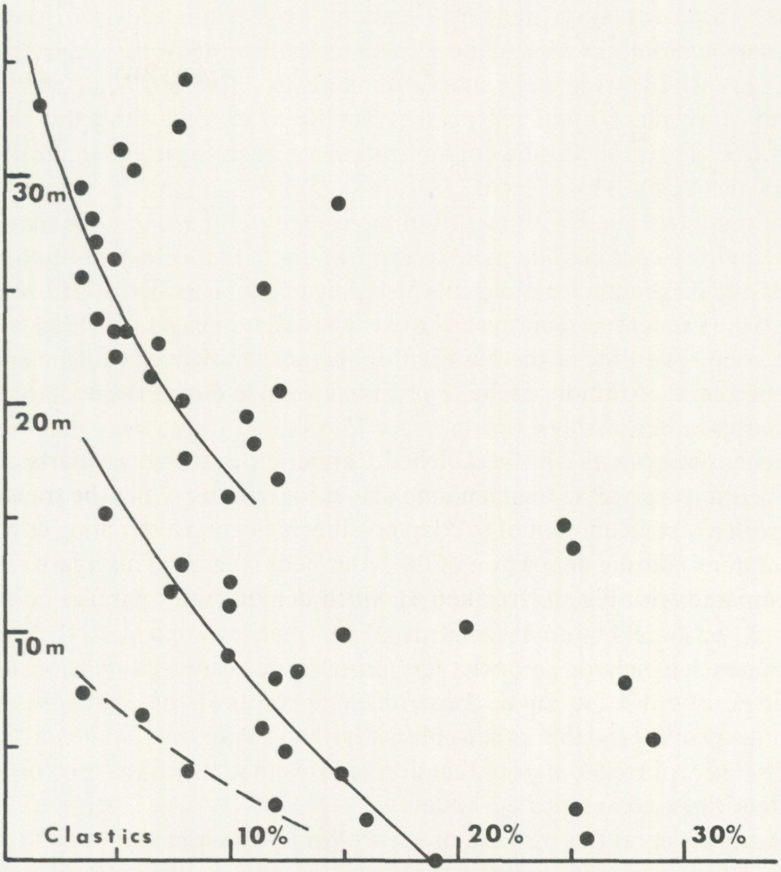

Fig. 3. Trends of the clastic components at Slitebrottet 1.

highest in the Upper beds but the number of samples having no non-clastic insolubles in the Upper beds is 18% as compared to 63% in the Lower beds.

Phosphorus occurs in small amounts (0.003 to 0.015%) throughout the section. It does have higher values in the two lower bentonitic zones (0.014%). Mean values for each of the three stratigraphic units excluding the bentonites are the same (0.007%). The occurrence of phosphorus in the bentonitic beds, which must have accumulated more rapidly than the limestones, seems difficult to explain unless numbers of organisms were killed by an influx of ash and the phosphorus from their remains incorporated in the sediments. There is no real evidence for this although there are chitin fragments in the residues, but the occurrence of chitin fragments is not unusual. On the other hand, it may more probably indicate some sort of ion-exchange phenomenon.

One question which must be addressed at this time is the role of certain elements other than calcium in the genesis and diagenesis of carbonate sediments. These accessory metallic elements, magnesium and iron, occur in significant amounts in most of these rocks and undoubtedly play an important part in events following the primary carbonate precipitation. What interpretation may we place upon the presence of these elements and the varying quantities? Their role during dolomitization has been suggested in the discussion of the Visby Beds.

The first question is with regard to the source of the magnesium and iron. Seawater itself contains adequate concentrations of these elements in solution to fuel any diagenetic reactions in which they might be involved. The percentage of magnesium in seawater is greater than that of calcium. Undoubtedly there are large stores of these and other metallic and non-metallic elements adsorbed on the surfaces of finely divided insoluble clastic materials such as clays, silts, and possibly even the very fine sands. It probably makes little difference whether these finely divided materials are quartz silts or clays, provided surface areas are abundant. The various forms of bonding probably consist of:

(a) Physical adsorption on the abundant surfaces of an insoluble colloidal or semi-colloidal material. (Meta-colloid).
(b) Ion-exchange bonding on the surfaces of certain clays. The elevated levels of easily strippable magnesium, iron and phosphorus of weathered bentonites would probably fall in this category.
(c) The incorporation of polyvalent metallic elements into the matrix of the clays themselves.
(d) Adsorption on the surfaces of non-colloidal materials.

Distinctions between these various types of bonding are hardly clearcut and it is probable that one type grades into another imperceptibly.

We have plotted the amount of magnesium and iron against the amounts of clastic insoluble residues a number of times and the frequent linearity of this relationship in many cases can leave no doubt as to the relationship. The most probable reason, is that polyvalent metallic ions such as Mg^{+2}, Fe^{+2} and Fe^{+3} can serve as precipitants for negative colloids such as clays and in the process are precipitated themselves. The clays and finely divided materials can then become a further "sink" or source for these elements in the subsequent diagenetic or epigenetic processes even when free access of sea water or its circulation is no longer possible in the sediments.

With regard to the active role of these elements the most likely surmise, if they do play an active role, is that they in some way participate in the process of dolomitization. Magnesium obviously is a major participant but the role of iron is more obscure. One point that seems amply clear is that the amount of iron present frequently is related to the degree of dolomitization. In fact, the classical potassium ferricyanide test for dolomite assumes a priori the presence of iron in all dolomites, since it is actually a test for iron. (Weathered limestones may give the same reaction so the test is only valid for subsurface samples.) As a consequence, we have frequently utilized the ratio of MgO/FeO as a criterion in interpreting the degree of dolomitization and formation of magnesian limestones containing clastics.

There are of course objections to this. The principal ones revolve around the possibility that weathering will produce HCl-soluble iron minerals by oxidation of sulfides and the consequent analyses for iron would obscure the relationship between iron and magnesium in weathered samples. Solution of the specimen in 1.0 Normal HCl as used in the analyses described here does not dissolve measurable (by ordinary means) amounts of iron from iron sulfides. Generally, however, we do believe that most of our FeO analyses give reliable values for iron from relatively unweathered carbonate fractions. Classical *whole* rock analyses on the other hand are of little value in the solution of the above relationships since the result will include all of the various iron minerals present regardless of original form. This will undoubtedly include considerable iron which was no bearing on the dolomite problem.

Our method of analysis may include some iron and magnesium stripped from the fine clastics, particularly in the colloid-size range during the solution of the carbonate. This, however, we feel to be usually insignificant. This iron has most probably been present throughout the entire history of the consolidated sediment and has been available to participate in reactions.

The next point for consideration is the form in which magnesium exists in the carbonate, i.e., the magnesium which is not bound by a nonstoichiometric bond to the various finely divided clastic materials present. It appears that it may occur in small amounts in solid solution in the calcite (Pettijohn 1957). In effect, some of the Ca atoms are replaced in the crystal matrix by magnesium. It may also occur that $MgCO_3$ or $MgCO_3 \cdot CaCO_3$ can exist simply as a separate mineral physically intermingled with calcite.

This process of "dolomitization" may be either syngenetic or diagenetic. It may at times be an epigenetic (tectonically related) process resulting from post-consolidation circulation of magnesium-containing waters through fracture zones. This type of dolomitization is usually localized and easily recognized and has not been found by us on Gotland.

Many pure dolomites do appear to have been formed diagenetically, but the silty and argillaceous magnesian limestones of Gotland may well have been formed during either the syngenetic or diagenetic phase of their history, probably the former with seawater as the source of the magnesium.

We have not encountered many true dolomites in materials collected on Gotland and no pure dolomites but have found rocks of an intermediate composition. The classification of these rocks merits discussion. There are, however, some clastic rocks in the Visby section (Ireviken 3) with CaO/MgO values lower than 3.96 as noted in the discussion of these beds.

Many rocks have been referred to as dolomitic limestone and it has been pointed out by Pettijohn (1957, p. 417) that rocks with "more than 10 but less than 90 per cent dolomite are comparatively rare". In consideration of the dearth of pertinent analytical data it might be difficult to substantiate this on a world-wide basis. Rocks with a CaO/MgO ratio greater than 24.47 would theoretically contain less than 10 per cent dolomite and the ratio would have to fall below 3.96 to indicate more than 50 per cent dolomite. Many of the Slitebrottet rocks have ratios above 24 and should probably be designated as *magnesian limestones* which in view of current uncertainties is a better term than dolomitic limestones. However, among the 26 samples from the lower part of the Slite section at Slitebrottet 1 there are 11 samples with CaO/MgO values between 3.96 and 24.47 indicating carbonate fractions with greater than 10% dolomitization.

In the northeast part of Slitebrottet 1 and above the deep pit there is an abandoned quarry face exposing 2.65 meters of thickly bedded limestones belonging to unit g. These are similar in general appearance to the bedded and biohermal limestones described by Hede (1960, pp. 64–65) at Lännaberget. These beds are separated by cover from the large quarry and sampling across the contact between Slite Marl and unit g was not possible.

The insoluble residues are low (mean = 0.9%) and consist primarily of silt and clay with a small amount of flaky silica at the base and pyrite at the top of the section. Chemically, these rocks are pure limestones with only minor amounts of magnesium and iron. Phosphorus is high, at the very top, but this could have resulted from contamination due to its location near the shore and probability of visitations by water fowl.

This exposure demonstrates the repeated tendency of the Gotland strata to trend upward from higher to lower clastic content. This tendency, although of relatively frequent occurrence, is not necessarily cyclical. (See also Table 4.)

SVARVARE 1 – Two specimens from the exposure at Svarvare 1 were analyzed. Laufeld lists two facies in the "Slite Marl" at this locality, the *Pentamerus gotlandicus* Beds and the Slite Siltstone. Our analyses are in agreement and also indicate two distinct lithologies. One is a very fine crystalline light grey limestone with some intermingled variably crystalline brown fossiliferous limestone. This has no determinable clastics but does have 39.9% secondary silica with some spongy porosity. There may possibly be a small amount of silt in the finer fraction. The CaO/MgO ratio is 7.1 and the MgO/FeO ratio 2.6.

The other sample contains 24.6% silt with only traces of clay. There is some disseminated pyrite and scolecodont fragments are present. The CaO/MgO ratio is similar to that of the other sample 7.4% but the MgO/FeO ratio is very high at 24. Both of the samples are exceptionally high in phosphorus, the sample with silt having 0.046% and the other 0.054%. The similarity of these figures combined with the differences in the facies raises the possibility of contamination, although this has not generally been a problem with this element.

FOLLINGBO 3 – The rock belongs to Slite Marl, northwestern part, and is predominately a finely crystalline, very fossiliferous limestone with argillaceous surfaces covered with bryozoans. The somewhat worn condition of the bryozoans suggests the possibility that they were reworked under conditions of mild mechanical energy.

The insoluble clastic fractions comprise only 4% of the total rock and consist of slightly argillaceous silts and medium light grey clays. Chemically, the rock is a limestone with an average CaO content of 52.16% and MgO of 0.74%. The FeO level is low, averaging 0.14%. Phosphorus is in normal amounts for limestone ranging from 0.003% to 0.019%.

MULDE 1 – This small exposure of the "Slite Siltstone" was described by Hede (1960, pp. 73–74) and subsequently by Laufeld (1974b, p. 102) and was considered by them to be in the upper part of the Slite Group. Our analysis of a single sample of this fine to medium crystalline light tan silty limestone or "siltstone" indicated 18.1% of insoluble clastic materials, mostly somewhat argillaceous silt with a little very fine sand. The CaO content was 38.42% and the MgO was 5.69% for a CaO/MgO ratio of 6.8 well indicating a magnesian limestone. Phosphorus is unusually high, 0.083%.

BARA 1 – Slite biohermal rocks are exposed at Bara 1 where they are overlain by the Bara Oolite of the Halla Beds. The biohermal material consists of light greenish to brownish dense to very finely crystalline rock with pink bryozoa and pelmatozoan debris as well as other fossils. Insoluble clastics average 5.7% and are mostly silty clay with a little very fine sand in one sample. Non-clastic insolubles are very small averaging 0.1% of secondary silica. Arenaceous Foraminifera were present in one sample.

Chemically the biohermal rock is a fairly pure limestone with a CaO/MgO ratio of 7.37. The effect of even a small percentage of fine clastics on the FeO content is evident when compared with limestones of reef or massive type with a low content of these fine mechanically-derived materials. A difference of approximately 5% in the amount of fine clastics appears to have increased the iron content by about 0.20 between these two types of rocks (Table 4). The small increase in the amount of phosphorus may be a coincidence, however, there is a marked difference in this respect between the two biohermal masses.

It would be pertinent to know just how much fine clastic sediment biohermal

TABLE 4. Comparison of the Slite bioherm at Bara 1 with similar beds.

	Means			No.
	% C	% FeO	% P	samples
Bara 1, Slite Bioherm	5.7	0.31	0.011	3
Slitebrottet 1, Massive Beds, Slite Beds, unit g	0.9	0.11	0.009	4
Högklint Biohermal Beds, Ireviken 3	1.0	0.07	0.004	6

development can tolerate. In times of storm reef organisms certainly have to contend with waters turbid with non-clastic sediment. This probably takes place in most cases over only a short period of time, whereas an influx of even a small amount of fine clastics might be more or less a permanent situation.

MULDE BEDS

The Mulde Beds are not present on the eastern side of the island, and our only specimens were collected at the Blåhäll 1 locality, where two meters of section are exposed. A total of 7 representative samples were collected. In the exposure and under low magnifications the rocks appeared to be fossiliferous, somewhat calcareous shales and argillaceous limestones. As in several other sections, there is an intermingling of two intimately related lithologies involving a difference of degree rather than of kind.

Four analyses of limestones average 30.1% clastics, primarily slightly argillaceous silt, and three analyses of calcareous shales average 62.4% of similar material. This difference does not suggest any significant change in the general milieu and the exposure could be considered to include but one facies as shown by a spread of only 32.3% between the means of the clastic values. Probably there was rather uniform carbonate deposition proceeding simultaneously with silt and occasional showers of clastic material.

The average CaO content of the limestones was 33.80% and the average MgO was 2.00%. The corresponding values for the shales are 11.25% and 3.14% respectively. As in other sections we find an increase in MgO content with an increase of insoluble material. It is even more obvious when the mean of the CaO/MgO ratios for the three samples of calcareous siltstone (3.6) is compared with that for the four samples of silty limestone (16.7). The carbonate in the shales is a dolomite.

The FeO level for the limestones averaged 0.80% as contrasted with 1.27% for the shales. This is exactly the same increase as noted for the MgO, namely, both MgO and FeO are 1.6 times as high in the siltstones as the limestones.

The amounts of phosphorus also tend to be related to the insoluble content ranging between 0.018% and 0.038%. However, phosphorus content does tend to increase downward in the section. Data from other trace elements would be of interest. These data strengthen the argument that the amount of dolomitization may be controlled by the amount of fine clastic sediment deposited which influences the FeO and MgO content.

HALLA BEDS

The Halla Beds overlie the Slite Group, thin southwesterly and disappear before having reached the west coast of Gotland. Our only opportunity to sample them was at Bara 1, the type locality for the Bara Oolite, where only a few decimeters of the thin-bedded rock occur in a small quarry. A sample of loose material was also obtained at a higher elevation where there had been digging to set a telephone pole. As these beds are draped over the flank of a Slite reef which rises above them the quarry and the loose material are probably stratigraphically closely associated.

The limestone is very light brown with ooids ranging in size from 0.1 to 2 mm. Although ooids are numerous there are also fossil fragments with thin calcareous coatings. Bryozoa and pelmatozoan columnals are present. The interstitial carbonate is very finely crystalline and there is also some secondarily recrystallized calcite. The residues are small averaging 2.4% and most of this is clastic material which ranges from a little very fine angular sand and silt to greyish brown clay. The small amount of non-clastic insolubles is silica with traces of pyrite. This rock was probably formed in shallow water when gentle wave action was an important influence.

Chemically it is a reasonably pure limestone with a CaO/MgO ratio ranging from 90 to 103. Iron is fairly high varying from 0.17% to 0.33%.

Our data justify no comment beyond this brief description of the lithology. Unfortunately this occurrence is not typical of the whole Halla section.

INTERPRETATIONS AND CONCLUSIONS

The true nature of sedimentary rocks cannot be determined by gross appearance and general description. This is particularly true where there are mixtures of carbonates and fine clastics. Relatively small amounts of carbonates may completely mask the presence of clays or fine tephra and so-called shales frequently are in fact limestones or dolomites. Relatively pure dolomites and limestones can usually be rather easily distinguished, but it is impossible to determine intermediate forms by appearance. Chemical analyses of whole rock samples determine characteristics for commercial use but are entirely inadequate where geological interpretation and genesis are involved, because the results are a combination of both clastic and non-clastic fractions of the rock and are characteristic of neither. The chemical and biochemical elements should be determined chemically and the mechanical elements mechanically. Even though a certain amount of estimate is inevitable, reproducible quantitative results can be obtained. Although only incidental to the present writing, the complete interpretation requires the determination of both the taxonomy and the ecology of any fossil organisms present as well as the mechanical and chemical data and this must be done by several types of specialists. Only when these things have been accomplished can a proper balance be achieved between genesis, biostratigraphy and lithostratigraphy. All of these are essential to a proper interpretation of the rock in both its local and regional setting.

With a few exceptions, the great bulk of the non-clastic elements in sedimentary rocks are produced internally, that is, within the environments of sedimentation or diagenesis. We consider diagenesis to involve those changes which take place below the interface between the sediment and the environment above, but only to the extent that permeability allows circulation of the medium in which the sediments are deposited. Although epigenetic dolomites occur and syngenetic dolomites are formed in rather specialized environments, it appears that many dolomites are diagenetic and that the source of the magnesium is seawater circulating below the interface. This is not true of most of the Gotland dolomites and magnesian limestones. Silicious materials may be deposited syngenetically and may be either biochemical or clastic. They are frequently reorganized after deposition and this is particularly true of the older rocks. Most of the minor and trace elements also have an ultimately syngenetic origin although reorganization may take place at any stage in the history of the rock.

The true clastics have an external origin, that is, they are introduced mechanically from outside the environment of deposition. We think of them as materials which were formed at another time and in another environment from the immediate environment of deposition. This excludes intraformational materials and the so-called bioclastics which are in the traditional sense not truly clastic. The clastics involved in the present study appear to be of two types. Either they have been derived mechanically by currents of wind or water from the area of provenance, that is, an area of supply outside the immediate area of deposition, or they consist of fine tephra which, judging by its character, also came from some distance away. Some of these originally may have been deposited in the area of provenance and undergone certain amounts of reworking so it would seem that both currents of wind and currents of water may have contributed to their introduction into the sediments. Time-honored interpretations have placed much emphasis on the tectonic behavior of the area of provenance to explain the characteristics of sediments. When sedimentary rocks are coarse and thick its behavior is thought to have been positive and when they are finer, thinner or nonexistent it is interpreted as negative or neutral. The significance of climate has been largely overlooked, and it would appear that the wind pattern and the amount of wind, the amount of rainfall and the resulting run off would have fully as much importance as the actual tectonism in the area. In consideration of the present state of the art we do not have the temerity to propose any suggestions as to the distances which either tephra or other clastics have travelled during the Silurian of Gotland. The number of variables involved do not permit this type of speculation.

There is a very definite relationship between the character and amount of the mechanically derived materials and the chemistry of the soluble portions of the rocks. Geologists as a group have been careless in their use of the word energy and as frequently used in geological literature it applies only to mechanical energy. It must be understood that there are also areas of high chemical energy and that this may be related not only to the characteristics of the medium of sedimentation but that considerable chemical energy may be introduced in purely clastic sediments in areas of low mechanical energy. This is normally related to the surface areas of the sediments and is therefore greater in the fine sediments. Where clays are involved, their physical chemistry and structure may also be an important factor. In an area such as Gotland, where fine clastics are frequently an important constituent of rocks, this is a considerable factor which has been discussed appropriately. In general, it may be stated that the greater the amount and the finer the clastic sediments the larger the amounts of magnesium, iron and phosphorus precipitated. This is probably also true of other trace elements not determined in the present study. The correlation between the amount of dolomitization and the percentages of fine clastics in both the Visby and the Slite sections is apparent. Reference to the text will show that greater amounts of FeO and phosphorus can also be frequently correlated with the characteristics of the clastics. This situation is not unique with the formations currently discussed.

Although many of the exposures studied were not thick enough vertically to allow adequate sampling, we believe that the analytical data give a reasonably fair picture of the overall character of the section. At least two sections were thick enough to permit the development of certain very definite trends. The approximately 15 meters sampled at Ireviken 3 exhibit a definite trend from higher clastic content with more argillaceous beds at the base to lower clastic content with more limestones at the upper part. Only the higher portions of the reef exposure could be sampled, but in these samples clastics were negligible. This may be entirely due to reef growth above the general level or the interface and should not be considered as a continuation of the trend to an extreme situation. The same type of trend is well-developed at Slitebrottet 1 where approximately 34 meters of section are exposed, and where massively bedded limestones exposed a few meters above the quarry have characteristics similar to those of the reef at Ireviken 3. It appears that the massively bedded limestones and the biohermal rocks have a great deal in common. It is possible that they are the climax of the trends as outlined. As there is a definite relationship between the chemical and the clastic characteristics, it might be expected that some of the trends developed in the chemical data are similar to those exhibited by the clastics. This is true in both cases.

The low angle nonconformity at locality Galgberget 1 shows evidence of mild tectonism. Both the physical and chemical characteristics of the sediment at the contact are perhaps more striking than the low angularity. This mild tectonism did not change the general milieu of the area to any great extent.

It appears that the beds included in the present paper followed a regular pattern with no profound breaks in the overall paleogeographical progression. There are some repetitive tendencies but these are not sufficiently pronounced to suggest cyclical events.

ACKNOWLEDGEMENTS

We appreciate the assistance of Gary Mosher who arranged for the x-ray diffraction analysis of some specimens by the laboratory of the American Foundrymen's Association, Des Plaines, Illinois. We are grateful to Ivan A. Flodin for many discussions regarding the statistical treatment of the data and for suggestions regarding graphic presentation of them. We are indebted to the officials of the Cementa Company for their cooperation in enabling us to sample the quarry wall at Slitebrottet 1. We are particularly grateful to Professor Anders Martinsson, Uppsala University, Dr. Lennart Jeppsson of Lund and Dr. Sven Laufeld, at that time also of Lund, among others, for guidance on a comprehensive survey of important localities over the Island. Without this introduction to the geology, our field work could not have been accomplished.

REFERENCES

GRAY, J., LAUFELD, S. & BOUCOT, A.J., 1974: Silurian Trilete Spores and Spore Tetrads from Gotland: Their Implication for Land Plant Evolution.–Science 185, 260–263.

HEDE, J.E., 1960: The Silurian of Gotland. *In* G. Regnell & J.E. Hede: The Lower Palaeozoic of Scania; The Silurian of Gotland. – Int. Geol. Congr. XXI Sess. Guide Exc. A 22 and C 17.

HEINRICH, E. WM., : Microscopic Identification of Minerals. – McGraw-Hill Book Co., 101–104.

LAUFELD, S., 1974a: Silurian Chitinozoa from Gotland.–Fossils and Strata. No. 5.

LAUFELD, S., 1974b: Reference Localities for Palaeontology and Geology in the Silurian of Gotland.–Sver. geol. unders. C 705.

LILIENTHAL, R. T., 1972: A Trace Element Analysis of Silurian Carbonate Rocks.–Unpublished M.S. thesis. Wayne State University, Detroit, Michigan.

MANTEN, A. A., 1971: Silurian Reefs of Gotland.–Developments in Sedimentology, 13. Elsevier Publishing Co.

MOSHER, R.E., 1972: Geochemical Stratigraphy from Microsampling in Niagaran Stratigraphy, Hamilton, Ontario.–*In* Guidebook for Mich. Basin Geol. Soc., Annual Field Excursion. 79–86.

MOSHER, R.E. & SANFORD, J. T., 1978: The Collection and Quantitative Analysis of Sedimentary Rocks for Stratigraphic Purposes.–*In* Mich. Basin Geol. Soc., Special Paper, No. 3. 107–111.

PETTIJOHN, F. J., 1957: Sedimentary Rocks, 2nd, Ed. Harper & Ron, Publ., N.Y. 718 pp.

SANFORD, J. T., MOSHER, R. E. & FRIEND, J.E., 1968: A Quantitative Study of Silurian Rocks from the Michigan Basin.–Geol. Assoc. of Canada, Proceedings 19, 37–44.

SEIWELL, H. R. & SANFORD, J. T., 1935: Phosphatic Nodules in Silurian Sediments of Western New York. (Abstract).–Geol. Soc. Amer. Proc. 362, June 1935.

VINOGRADOV, A. P., 1953: The Elementary Chemical Composition of Marine Organisms. –Memoir Sears Foundation for Marine Research. Number II. New Haven, 1953.

PRISKLASS A

Distribution
Liber Distribution
162 89 STOCKHOLM
Tel 08-739 91 30

Fotosats: Ord & Form AB
Tryck: Offsetcenter ab, Uppsala 1985

ISBN 91-7158-340-8
ISSN 0082-0024