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METAL SORPTION BY CARBONATE ROCKS
AS INFLUENCED BY THEIR CHEMISTRY

A Thesis

Submitted to the Faculty of Graduate Studies Through
the Department of Geology in Partial Fulfilment of
the Requirements for the Degree of Master of Science
at the University of Windsor

By

Sunand Shadrach Mabbula

Windsor, Ontario

1978

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ABSTRACT

This study is an investigation of the relation between the chemical composition of carbonate rocks and the adsorption of copper, lead and zinc. The following constituents have been determined on 121 carbonate rocks: CaO, MgO, Al₂O₃, SiO₂, loss on ignition and acid insoluble content. These samples were collected from quarries in southwestern Ontario. This study is an extension of earlier work (Garber, in preparation) where 92 of the above 121 samples were investigated to determine the relation between metal adsorption and water sorption. Statistical analysis of the data revealed numerous significant correlations.

The following relationships were observed: a direct relationship exists between water, copper, lead and zinc sorption and alumina content of dolomites. Inverse relationship in dolomites between metal sorption and MgO content is due to decrease of Al₂O₃ and increase of MgO in progressively purer dolomites. Lack of correlation between CaO content of dolomites and metal sorption suggests that calcite in dolomites is reactive with metals and masks physical adsorption. Correlation between water and metal sorption of dolomites suggests that metals are concentrated by physical adsorption in dolomites. In limestones the lack of correlation between lead and zinc sorption and MgO, CaO and Al₂O₃ is due to chemisorption. The direct relationship between water sorption and alumina content of limestones and lack of correlation between lead, zinc and alumina in limestones indicates that in limestones the metal ions of Cu, Pb and Zn react with the rock likely forming their own minerals. There is no relation between concentration and internal surface area. Correlation between copper sorption and alumina content in limestones suggests that impure limestones can adsorb and concentrate copper.

ACKNOWLEDGEMENTS

I gratefully acknowledge Dr. P.P. Hudec who suggested this topic of research and supervised much of this work. In addition I thank Dr. A. Turek who was a co-adviser in this study. This study follows a thesis in progress by Mr. J. Garber, and the time adsorption experiments were made by Mr. J. Garber. I thank Mr. Garber for allowing me to utilize his adsorption experiments data for the present study.

I also extend my thanks to Dr. C. Riddle for assistance with X-ray work, and Dr. M. Stupavsky and Mr. G. Marzetti for their help with computer treatment of data.

CHAPTER 1

INTRODUCTION

The purpose of this study was to investigate the sorption of water, Cu, Pb and Zn by carbonate rocks as a function of their bulk chemical composition. Moreover, this study is an extension of the work of Garber (in preparation) who investigated the phenomenon of metal sorption by carbonate rocks as a function of time. This study involved chemical analysis of 121 carbonate samples collected from quarries in southwestern Ontario. 115 samples are the same as used by Garber. Chemical constituents determined in this study were CaO, MgO, Al₂O₃, SiO₂, LOI and acid insoluble content. This data is correlated with the adsorption measurements made on the same samples by Garber.

The chemical analyses are a reflection of the mineral composition of the rock. The CaO and MgO content are due to calcium carbonate and dolomite. The alumina content and silica content are a measure of the clay content in the rock and similarly the acid insoluble also a measure of the clay content. Thus the adsorption data can be directly related to the chemical composition of the rock and indirectly to the mineralogy of the rock. The clay content of carbonate rocks (1% to 27%) plays an important role in physical adsorption of water and metals, since clay surfaces are more water adsorptive than calcite and dolomite surfaces (Grim and Cuthbert 1945, Rosenquist 1955, Mason 1956). In nature clay minerals are important in adsorption and concentration of metals from sea-water e.g. the blue-green muds of continental slopes. This aspect has been experimentally demonstrated by Krauskopf (1956). He has shown that copper, lead, zinc and other metals from sea-water could be adsorbed by clays in significant quantities. According to Dunham (1964) the Kupferschiefer of Northern Europe is a bituminous calcareous shale and the ore deposit may possibly be related to adsorption

4

of metallic elements from sea-water during the slow accumulation of sediments or subsequent diagenesis. White (1968) discussing the Red Sea geothermal system (natural solutions in the process of ore formation) reports that the dominant clay minerals of the Red Sea sediments is a mixed layer of illite-montmorillonite and the analysed samples contained 0.5% Cu, 0.15% Pb and less than 2.6% Zn. Thus clay minerals may play a major role in nature in adsorption and concentration of the metals from sea-water. Similarly the clay minerals in the carbonate rocks may play the same role in adsorption of metals. Therefore, the present study deals with the adsorption of metals as influenced by the rock chemistry particularly alumina content, which is a measure of the clay content.

The clay minerals have an important function in natural water systems because of their large surface area per unit weight. Boyd (1971) reported the surface area for several clays as follows: kaolinite $13.2 \text{ M}^2/\text{g}$, montmorillonite $85-800 \text{ M}^2/\text{g}$, illite $120-350 \text{ M}^2/\text{g}$, dolomite $0.743 \text{ M}^2/\text{g}$ and calcite $0.714 \text{ M}^2/\text{g}$. The adsorption of metals by clay minerals in the continental slopes is well known; the clay minerals act as natural depoisoning agents. Without their actions seas would contain toxic levels of several metals e.g. Se, Cu, Pb (Krauskopf 1956). Adsorption by clay minerals can be physical or chemical, this study is mostly concerned with physical adsorption.

Review of literature indicates that the lead-zinc ores of Mississippi Valley type and Alpine type deposits have more affinity for dolomites than for limestones (e.g. Geldsetzer 1971, Callahan 1967, Smirnov 1967 and Schneider 1953). Thus this study is relevant to this observed association of lead-zinc deposits and dolomites. Garber has shown that there is a relationship between water adsorption and metal sorption to some extent. His study dealt with metal sorption as a function of time. Garber's study

evolved from the observation that carbonate rocks have varying affinity for adsorbed water, i.e., the amount of water adsorbed on the internal surfaces of the rocks is a function of that rock mineralogy. In particular, the clay content of the rock has a profound influence on water sorption.

Water is a polar molecule, and in its sorption on to clay mineral surfaces, the positive or cat-ionic side of the water molecule is adsorbed. This assumption that highly sorptive carbonate rocks will also exhibit high sorptive capacity for metal ions has been supported by his experiments.

To test this hypothesis he has chosen copper, lead and zinc, since lead and zinc are common metal forming deposits in the carbonate rocks e.g. Pine Point. Copper also forms sedimentary deposits either in oxygenated environments in limy pelitic sediments, e.g. Redstone copper deposit or in euxinic, organic rich pelitic muds e.g. Kupferschiefer deposit. Garber performed his adsorption experiments using metals dissolved in distilled water and also some metals dissolved in 5% w/v NaCl solution. He has observed that lead and zinc show a similar behaviour under all circumstances studied and copper behaves in an opposite manner to that of lead and zinc, this may explain why copper on the one hand and lead and zinc on the other tend not to occur together in low temperature deposits of the Mississippi Valley type in sedimentary rocks. Probably this behaviour could be the influence of the rock chemistry and this aspect is considered in the present study.

As mentioned earlier Garber's work has been extended to an analysis of the major elements in order to correlate adsorption as a function of bulk chemical composition. Chemical analysis and Garber's 48 hour water and metal sorption data were statistically evaluated using an IBM 360/70 computer to check correlation between major constituents CaO, MgO, Al₂O₃ and water and metal sorption. Results of these statistical analyses are discussed and an

attempt is made to relate the laboratory experimental results to known lead-zinc deposits, particularly the Mississippi Valley lead-zinc deposits. It will be shown that lead-zinc adsorption experimental work indicates that lead-zinc deposits in carbonate rocks would preferentially form in dolomites since the limestones are more chemically reactive than the dolomites. This of course presupposes that adsorption can lead to the process of ore deposition.



CHAPTER 2

THEORETICAL CONSIDERATIONS OF IONIC EXCHANGE AND ADSORPTION

Carbonate rocks used in this study are mainly composed of calcite and dolomite. Quartz and clay minerals occur as accessories. The grain size of a mineral governs the internal surface area available for adsorption. Although the overall clay content of the carbonate rocks does not exceed 1% to 2%, clay minerals play an important role in adsorption of metals. Calcite, dolomite and quartz have low surface area compared to clay minerals. Dunn and Hudec (1965) presented evidence that the major non carbonate impurities such as clay and silica play a large part in sorption of water in rocks.

In this chapter adsorption and ion exchange phenomena of clay minerals, calcite and dolomite are briefly explained. Clay minerals are highly adsorptive because of their unique properties such as smaller grain size, large surface area and high surface charge. Two types of adsorptions are recognized: (a) Physical or Van der Waal's adsorption, and (b) chemisorption or chemical adsorption. Both types may act together, and all gradations between extremes exist. Physical adsorption is characterized by low heats of adsorption and by a loose bonding of the adsorbate to the adsorbent. Chemical adsorption or chemisorption, on the other hand, is characterized by high heats of adsorption and a strong chemical bonding (i.e., by valance bonds) of the adsorbate. It may involve the bonding of a foreign anion or cation, or both, to open bonds at the surface of the adsorbent. It may involve the exchange or substitution of a foreign cation or anion, or both, for a cation or anion at the surface. Base exchange may be considered as a particular type of adsorption. In base exchange, exhibited by clays, a cation

in the clay may be exchanged for another cations present in aqueous solutions in contact with clay minerals (Mason (1966). Physical adsorption is more common in clays and chemisorption is more common in carbonate minerals such as calcite. Cation exchange is a common and important phenomenon in clay minerals it is therefore discussed in more detail below

Cation Exchange in Clay Minerals

Structural Causes

The residual charge on a mineral grain is usually negative and therefore, attracts cations. The three mechanisms that are believed to be responsible for charge phenomena on clay mineral surfaces are (1) substitutions within lattice structure, (2) broken bonds and (3) hydrogen of exposed hydroxyls (Grim 1968).

Substitutions within the lattice structure of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of lower valence, particularly Mg^{2+} for Al^{3+} in the octahedral sheet result in unbalanced charges in the structural units of some clay minerals. Sometimes such substitutions are balanced by other lattice changes or frequently by adsorbed cations.

Broken bonds around the edges of silica-alumina units would also give rise to unsatisfied charges, which would be balanced by adsorbed cations.

The hydrogen of exposed hydroxyl ions (which are an integral part of the structure rather than due to broken bonds) may be replaced by a cation which may be exchangeable (Grim 1968).

Surface Area, Charge Density and Exchange Capacity

The three parameters of surface area, charge density and exchange capacity are somewhat related. Surface area and exchange capacity are

interdependent. Ormsby et al. (1962) found a linear relation between surface area and exchange capacity for kaolinite (Fig 1-A). Their results show that relatively high cation exchange capacity of poorly ordered kaolins is directly a result of high surface area. Van der Marel (1958) also showed an excellent linear relation between cation exchange and the surface area.

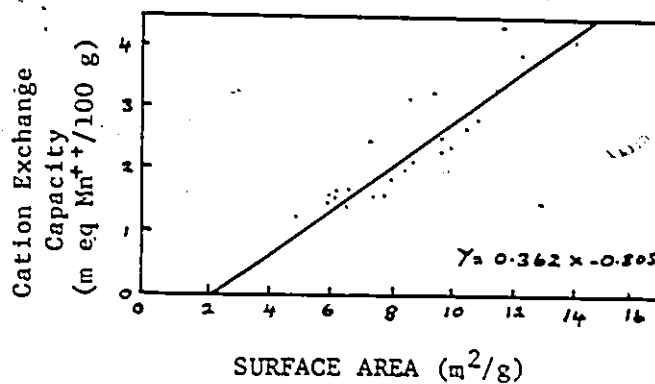


Fig. 1-A. Cation-exchange capacity-surface area (glycerol retention) relation for kaolins. (after Ormsby et al. 1962)

As surface area increases, the total charge density and exchange capacity should likewise increase (Wayman 1967). The mutual exchangeability of cations depends on their charge density (Wedepohl 1971). The number of adsorbed ions is numerically equal to the charge density in electric charges (Osipow 1962). A high charge density causes a strong binding of the cation to its hydration-shell.

Variation due to Particle Size

Cation exchange capacities of clay minerals increase as the particle size decreases. Particle size in turn is related to surface area. Decrease

in particle size increases the surface area.

Effect of Temperature

According to Kelly (1948) the temperature effect of cation exchange is generally small. Ion exchange is virtually independent of temperature, since surface charge varies very little with temperature (Osipow 1962). However, there appears to be controversy with regards to the effect of temperature on cation exchange. Sen and Guha (1963) experimentally showed that on heating a kaolinite clay to 1000°C , its cation exchange capacity showed no change until about 400°C . Above 400°C there was a sharp increase in cation exchange capacity to about 550°C followed by a gradual decrease then by an even more moderate decrease between 700°C and 800°C . The increase in cation exchange capacity is correlated with disruption of the kaolinite structure on dehydroxylation. The subsequent decrease in capacity suggests reorganization of bonding in the resulting product.

Effect of pH

Exchange capacity increases with increase in pH. Heydemann (1959) has shown experimentally that the adsorption of copper by various clay minerals increases with increasing pH as well as copper concentration (Figs. 2-A, 3-A and 4-A). In water either the Si-O or Al-O bonds tend to hydrolyse in the formation of weak acid (Si-OH) to form Si-O bonds. because of the weakness of Si-OH, the hydroxyl tends to ionize the Si-OH to $\text{SiO}^{-} + \text{H}^{+}$. This concept is most plausible under neutral and alkaline conditions, and it also explains why exchange capacity increases with increase in pH. Under acid conditions the metal to oxygen bond would tend to adsorb a hydrogen ion and neutralize the site. In acid solution, the surface may become positive through adsorbed hydrogen or other cations along with the

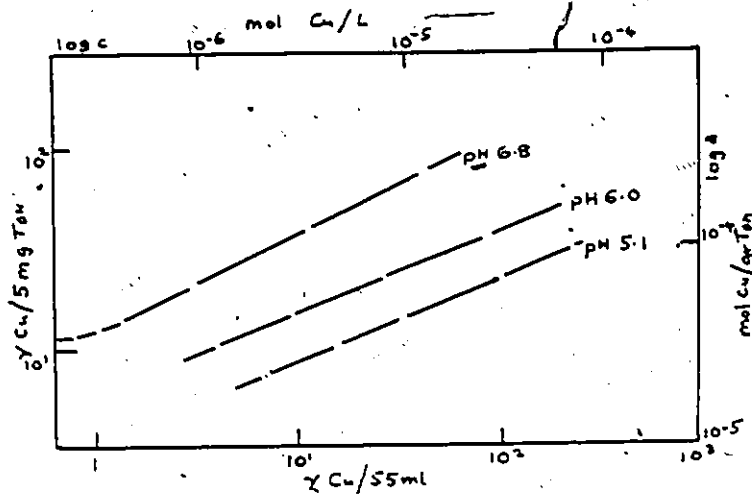


Fig. 2-A. Adsorption on illite (after Heydemann 1959)

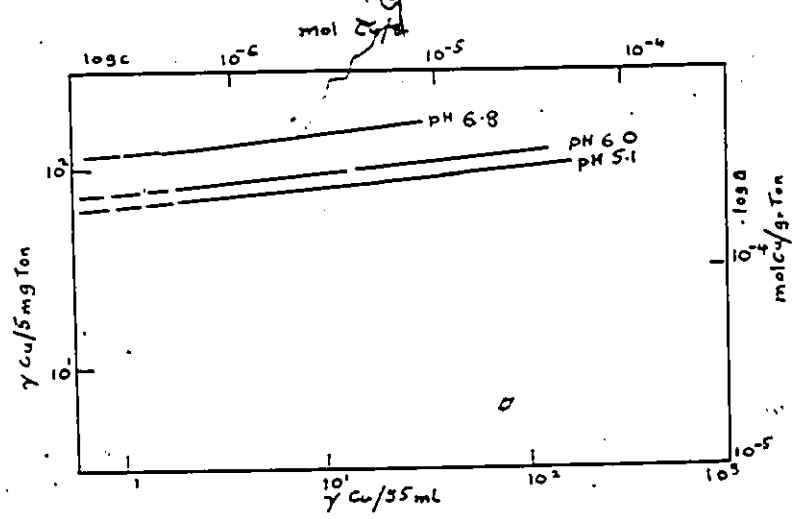


Fig. 3-A. Adsorption on montmorillonite (after Heydemann 1959)

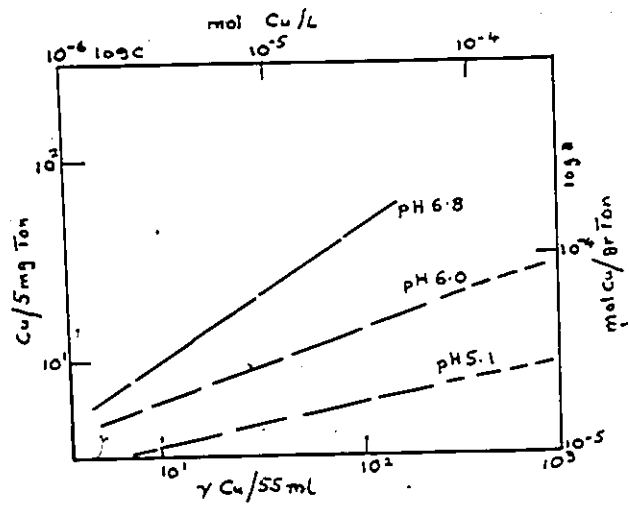


Fig. 4-A. Adsorption on kaolinite (after Heydemann 1959)

exposed cationic sites created from breaking bonds (Wayman 1967).

Effect of Concentration

The amount of substance adsorbed from a solution increases with its concentration in that solution (Glasstone 1950, Mason 1966). Similarly Kurbatov et al. (1951) reported that adsorption increases with increasing amounts of adsorbent and adsorbate. Hydemann (1959) has shown that adsorption of copper by various clay minerals increases with increased concentration of copper (Figs 2-A, 3-A and 4-A).

Water and Metal Sorption

Clays adsorb various amounts of water. Water has a natural tendency to condense on clay surfaces because of the water's dipole property and also because of the large surface area of clay minerals which is related to the sheet structure of clay minerals. Water is adsorbed by weak bonding forces on kaolinite and becomes more strongly bonded in montmorillonite. The essential difference is the character of the bond that probably results from the interlayer bonding in montmorillonite. The manner in which water vapour is adsorbed is expressed as energy difference: $U-A$, where U is the hydration energy and A is specific adsorption. The difference, $U-A$ is a function of the partial vapour pressure of water. If the difference is less than zero, it is assumed that water is retained only by weak Van der Waal's forces.

Krauskopf (1956) has experimented with the adsorption of thirteen rare elements in sea-water by clay and other adsorbents (the thirteen metals were: Cu, Zn, Pb, Cd, Hg, Ag, Co, Ni, Bi, Mo, W, Cr and V). The experiments were conducted at room temperature (18-23°C) and at normal pH range of sea-water (7.8 to 8.2). For clay, he chose two samples of montmorillonite

as these should show maximum adsorptive effect. His experiments revealed that Cu, Zn and Pb were adsorbed more strongly and more consistently than other metals. Hg showed a strong adsorption. Cobalt and nickel, likewise divalent elements, were much less effectively adsorbed. His explanation for the markedly smaller adsorption of Ni and Co as compared to Cu, Zn and Pb, despite the similarity of their ions may possibly be correlated with greater polarizing ability (greater chalcophile tendency) of elements with complete 18 electron shells. The very weak adsorption of Ag and V by most of the materials used may be because they form univalent cations. The elements Bi and Cd were not studied because of the analytical difficulties. Both, however, might be expected to behave like Cu, Zn and Pb. Krauskopf (1956) states that the amount of adsorption of metals in any particular case depends not only on temperature, pH, salinity but on time of standing, amount of physical state of adsorbent and concentration of the adsorbed ions.

Adsorption by Calcite and Dolomite

Solids which are negatively charged in water, such as silica, readily adsorb cations (Osipow 1962). Calcite and dolomite form crystals and the perfect crystal is electrically neutral. Calcite and dolomite crystals in the carbonate rocks may have unsatisfied bonds on their broken edges, and these are probably balanced by adsorbed foreign cations.

Thermodynamic studies of zinc sorption on calcite, dolomite and magnesite by Jurinak and Bauer (1956) revealed that about 10% of the adsorption sites probably available on calcite were occupied by zinc when equilibrium Zn^{++} aqueous concentration was $0.90 \times 10^{-6} M$ at $25.1^{\circ}C$. The Ca-magnesite showed somewhat greater affinity for zinc ion than calcite while dolomite

was intermediate.

Calcite is chemically a highly reactive mineral and therefore, adsorbs metals by means of chemisorption rather than by physical adsorption. This fact has been experimentally demonstrated by Heydemann (1959) and latter confirmed by Ashry (1973). Heydemann's experiments showed that copper is adsorbed by clay minerals and quartz according to Freundlich adsorption isotherm whereas in the case of calcite, a chemical reaction takes place. According to him calcite powder takes up copper ions from very dilute neutral aqueous solutions through a chemical reaction and not through adsorption as with clay minerals. Ashry (1973) analysed chemically the clay fractions of the Nile River sediments. He determined the copper and zinc contents by X-ray fluorescence and atomic absorption spectrophotometry respectively. He found that there is a correlation between copper and zinc adsorption and the analyzed clay-sized carbonate (calcite) particle size. The following figures (Figs. 5-A and 6-A) show correlation between Cu, Zn and CO_2 in the clay fractions. The correlations according to Ashry reveal that Cu and Zn were bound to the clay sized carbonate particles, and the bonding between the carbonate particles and copper and zinc takes place by a chemical reaction process.

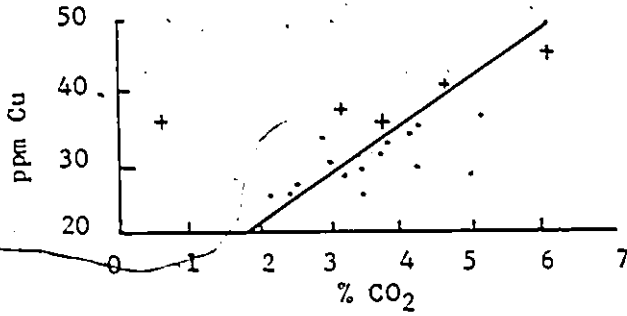


Fig. 5-A. Copper content vs %CO₂ of the clay fractions of the Nile sediments. . Subsurface delta sediments. + drainage valley sediments (after Ashry 1973).

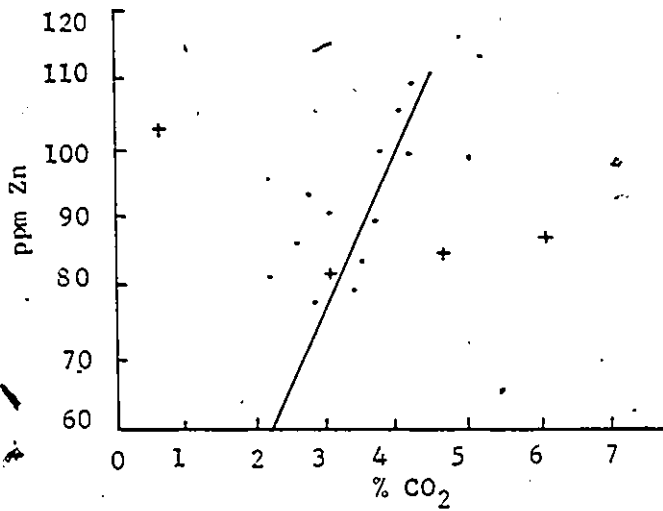


Fig. 6-A. Zinc content vs %CO₂ of the clay fractions of the Nile sediments. . Subsurface delta sediments. + drainage valley sediments (after Ashry 1973).

CHAPTER 3

SAMPLE DESCRIPTION

Samples for this study were collected by Garber in the southwestern Ontario from the following quarries:

Dufferin Materials and Construction Ltd; Hagersville (45)

Milton Quarries Ltd; Milton (78)

Norfolk Quarry Co; Port Dover (80)

Walker Brothers Quarries, Thorold (100)

Jarvis Crushed Stone Ltd; Jarvis (59)

Armstrong Brothers Co. Ltd; Vinemount Quarry (6)

Law, R.E., Crushed Stone Ltd; Port Colborne (62)

The numbers in the paranthesis are quarry numbers as assigned by Hewitt and Vos (1972). Fig. 1 gives the location of the above quarries.

A total of 121 samples was collected. These samples represent a wide range of carbonate rocks. Out of 121 samples 92 were used in this study, since Garber has conducted adsorption experiments on 92 samples only. Forty seven of these were classified as dolomites and 45 as limestones. Mineralogically the rocks contain calcite, dolomite, clay minerals, free quartz and glauconite. In some of the samples bituminous material is also found. The rocks are generally hard and brittle. They are Paleozoic in age and belong to the formations as shown in table 1. The petrographic descriptions are given in table 2.

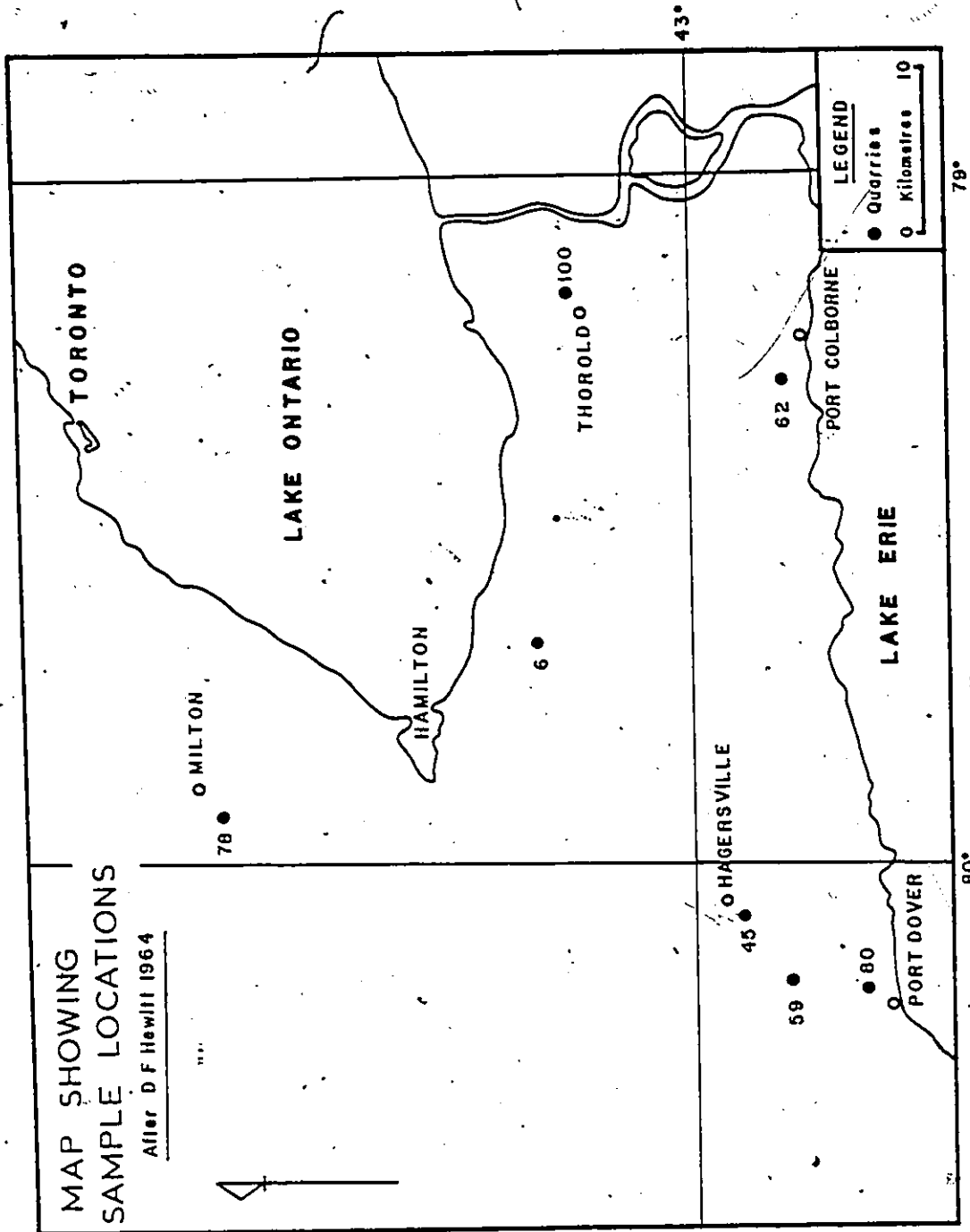


Fig 1 Sample locality map. Numbers are the quarry numbers as assigned by Hewitt (1964)

TABLE I
STRATIGRAPHY

Sample No. ⁺		Formation	Rock type
80 (1 to 10)		Dundee Formation	Limestone
59 (1 to 10)	Middle	Bois Blanc Formation	Cherty Limestone
62 (1 to 15)	Devonian	-,,-	-,,-
45 (1 to 20)		-,,-	-,,-
100 (1 to 5)	Middle	Lockport Formation	Gasport dolomite
6 (1 to 10)	to	-,,-	-,,-
100 (6 to 20)	Lower	-,,-	Goat Island dolomite
78 (1 to 5)	Silurian	Amabel Formation	Dolomite
78 (6 to 20)		Raynales Formation	Dolomite

+ Sample numbers are e.g. 80 (1 to 10) means sample 80.1, 80.2 80.10.

TABLE 2

PETROGRAPHIC DESCRIPTION OF SAMPLES

Sample No.	Description
80 (1 to 10)	Limestone; light grey colour, microcrystalline, with rare disseminations of bituminous material, often fossiliferous.
59 (1 to 10)	Limestone, light greyish brown colour, slightly silicious, microcrystalline with disseminated bituminous material.
62 (1 to 5)	Shaly limestone; medium brownish grey, microcrystalline with some fine dark grey bituminous material. Often shaly partings.
62 (6 to 10)	Limestone; medium brown colour, microcrystalline, silicious often contains glauconite.
62 (11 to 15)	Limestone; medium brown colour, fine grained, silicious, thin laminated with fine bituminous material.
45 (1 to 5)	Limestone; brownish colour, microcrystalline and silicious.
45 (6 to 15)	Limestone; light brownish colour, microcrystalline, silicious and fossiliferous.
45 (16 to 20)	Limestone; light greyish brown colour, microcrystalline, slightly silicious and shaly.
100 (1 to 5 & 20)	Dolomite; light grey, medium crystalline, calcareous with dominant crystalline calcite.
100 (6 to 19)	Dolomite; light grey, massive microcrystalline with dark grey bituminous material.
78 (1 to 5 & 16 to 20)	Dolomite, light grey to buff, medium to coarse crystalline, massive to medium layered, crinoidal, porous with vugs. Pore size ranges from 0.03 mm to 0.51 mm.
78 (6 to 15)	Dolomite; light and medium grey mottled, often buff, micro to medium crystalline, medium bedded with shaly partings. Porous with vugs.

WATER AND METAL SORPTION TESTS

The following is the brief description of procedure of water and metal sorption tests carried out by Garber.

Water Sorption Tests

The samples were crushed and divided into two groups: A and B. Group A was subjected to experiments referred to as untreated while group B samples were first immersed in salt solution with a concentration of 5% NaCl by weight; since base metal ore bearing fluids are Na-Ca-Cl brines, with total salt contents generally equivalent to 5-40 weight percent of NaCl (White 1968). For the present study only group A is considered. However, the presence of salt does influence the solubility of metals and also adsorption, and its effects are discussed below.

Both groups of samples were dried and water adsorption capacity was determined. The samples were placed in humidity chambers at room temperature ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$), and the humidity was maintained by saturated solutions of potassium thiocyanate (KCNS 45%). Relative humidity of 45% R.H was chosen as sorption indicator humidity, because it has been shown (Aylmore and Quirk 1962) that at this particular humidity one molecular layer of water covers the internal surface area and the 45% R.H is thus an indicator of the internal surface.

Garber's experiments have shown that there was no significant difference in water sorption between salted and unsalted groups at 45% R.H. He stated that it is not the presence of salt itself that increases the sorptive capacity of the rock, but the ionic exchange that takes place at the surface of the minerals, in particular clays that enhances the sorptive effect of the rock. The water of hydration for the salt crystals does not change the

45% humidity (Hudec personal communication 1977)

However, presence of salt influences the adsorption of metals from a solution. Hudec et al. (1976) have experimentally demonstrated that the adsorption of copper increases with increase in salinity while lead and zinc show a decrease of adsorption with increase in salinity. Moreover, they stated that as metal bearing brines become progressively diluted with surface phreatic waters, there will be a tendency for lead and zinc to drop out of solution, whereas copper will be taken up into solution from the surrounding rocks.

Metal Sorption Tests

Copper, lead and zinc were dissolved in solutions buffered at a pH of 5 in order to prevent chemical reaction with carbonate rock; e.g. copper at a pH of 5.5 would precipitate.

The concentrations of metal solutions were 200 ug/ml, 500 ug/ml and 100 ug/ml for copper, lead and zinc respectively. These were prepared in distilled water and in 5% NaCl solutions. The unsalted samples were immersed in a solution containing the three metals (Cu, Pb and Zn), the solution being prepared with distilled water. The salted samples were similarly immersed in the three metal solution, except that this solution was made up to contain 5% NaCl w/v. Both sets of samples and solutions were allowed to stand for 48 hours. The solutions were then analysed using atomic absorption to determine the amount of metal removed. Table 3 gives the analytical data of the unsalted samples (Garber, in preparation).

TABLE 3

WATER AND METAL SORPTION RESULTS (FROM GARBER)

Sample No.	H ₂ O%	Cu ug/g	Pb ug/g	Zn ug/g
45.1	.043	62.80	387.3	67.24
45.2	.139	90.48	397.12	61.97
45.3	.07	80.25	368.39	63.00
45.5	.078	124.45	323.44	65.45
45.6	.448	155.85	76.13	31.06
45.7	.076	141.63	396.01	71.82
45.9	.107	87.69	417.73	57.91
45.10	.075	100.07	379.74	65.98
45.11	.112	124.66	307.01	74.12
45.12	.140	121.05	421.32	73.14
45.13	.170	111.46	400.18	73.06
45.14	.135	104.19	429.90	71.55
45.15	.054	73.12	387.55	68.99
45.16	.021	114.65	389.27	72.01
45.19	.096	88.68	414.99	61.92
45.20	.112	109.38	382.13	66.13
78.1	.006	62.41	249.41	34.30
78.2	.054	50.12	276.10	19.57
78.3	.024	52.27	152.07	30.44
78.4	.031	64.68	299.09	36.78
78.5	.033	61.56	230.87	29.83
78.6	.052	53.04	270.30	35.56
78.7	.095	73.43	247.84	38.99
78.8	.060	54.20	225.74	32.02
78.9	.038	46.37	197.59	33.40
78.10	.067	56.39	292.66	30.65
78.11	.018	44.85	167.17	29.64
78.13	.049	46.82	222.92	31.44
78.14	.051	55.24	246.12	39.47
78.15	.051	52.92	241.27	38.38
78.16	.03	45.18	209.78	29.87
78.17	.025	58.59	210.74	32.90
78.18	.033	32.20	164.86	24.21
78.19	.045	58.14	230.92	29.78
78.20	.04	56.85	217.59	44.60
80.1	.019	134.65	319.96	73.68
80.2	.051	99.88	402.27	68.78
80.3	.030	92.21	393.46	30.53
80.4	.023	78.03	402.15	70.77
80.5	.036	98.28	400.41	72.67

TABLE 3 Continued

WATER AND METAL SORPTION RESULTS (FROM GARBER)

Sample No.	H ₂ O%	Cu ug/g	Pb ug/g	Zn ug/g
80.6	.031	60.25	397.12	71.03
80.7	.070	107.39	402.19	67.97
80.8	.020	104.01	391.4	72.87
80.9	.025	85.34	386.55	71.30
80.10	.04	89.19	416.04	74.58
100.1	.026	51.9	301.69	37.87
100.2	.032	57.51	269.56	35.34
100.3	.036	49.22	253.88	34.93
100.4	.031	43.86	210.99	33.25
100.5	.028	47.84	247.73	34.48
100.6	.241	94.46	349.92	44.61
100.8	.248	151.10	258.35	69.21
100.11	.149	83.15	392.22	60.74
100.12	.131	153.62	154.64	72.78
100.16	.086	90.70	381.78	49.98
100.17	.130	86.10	379.99	36.08
100.19	.288	129.87	411.17	35.30
100.20	.209	81.31	129.74	43.72
59.1	.035	61.09	396.87	75.82
59.3	.027	43.40	398.01	74.72
59.4	.050	68.49	421.76	73.41
59.5	.025	56.81	410.92	74.54
59.6	.021	76.97	414.32	32.82
59.7	.049	62.31	380.14	71.90
59.8	.017	52.97	413.34	72.46
59.10	.051	62.44	390.57	71.20
6.1	.096	58.34	288.86	30.23
6.2	.121	68.52	385.56	38.68
6.4	.264	81.87	345.24	56.08
6.6	.323	152.65	225.35	60.86
6.7	.243	103.60	324.35	53.90
6.9	.239	81.4	299.72	42.11
6.10	.278	82.16	298.99	44.70
6.11	.015	20.98	69.32	43.35
6.12	.175	100.67	215.52	54.48
6.13	.160	100.67	199.41	18.24
6.14	.044	55.28	139.61	30.72
6.15	.062	73.22	143.81	31.27
6.16	.024	19.61	55.24	12.64
6.17	.126	68.86	170.49	29.09
6.20	.037	43.52	139.01	26.18

TABLE 3 Continued

WATER AND METAL ADSORPTION RESULTS (FROM GARBER.)

Sample No.	H ₂ O%	Cu-ug/g	Pb ug/g	Zn ug/g
62.2	1.141	133.04	363.39	60.12
62.3	1.355	155.09	298.53	68.35
62.4	1.067	114.54	407.62	70.39
62.6	1.054	149.30	408.06	75.42
62.7	1.028	122.72	391.04	75.92
62.8	1.111	130.75	391.90	75.03
62.9	.970	80.20	306.84	55.59
62.10	1.082	85.31	433.49	47.22
62.11	1.135	115.04	404.40	58.92
62.12	.981	60.82	386.14	62.73
62.14	1.114	122.19	400.44	60.23

CHAPTER 4.

CHEMICAL ANALYSIS

Preparation of Samples for Analysis

Rock samples were washed and dried and then crushed using a jaw crusher; the crushed samples were pulverized using Broun pulverizer to a -120 mesh. Each sample was homogenized by rolling. To avoid contamination all equipment was cleaned after each sample was crushed.

Preparation of Solutions for Atomic Absorption and Rock Powder Pellets for X-ray Fluorescence

CaO, MgO, Al₂O₃, SiO₂, loss on ignition and acid insoluble content were determined for all 121 samples used in this study. Atomic absorption was used for the determination of CaO and MgO. X-ray fluorescence method was used for the determination of Al₂O₃ and SiO₂.

For atomic absorption determination of Ca and Mg and also for the determination of acid insoluble the sample was dissolved as follows. About 1 g. of rock powder was weighed out accurately into a 100 ml beaker. 20 ml of 6N HCl was quickly added to the rock powder. The sample was covered with a watch glass to avoid spluttering. The beaker and the contents were heated for about one and a half hours at about 250°C. Precaution was taken not to allow the contents to boil or evaporate to dryness. After heating, the beaker and contents were allowed to cool. The solution was filtered through number 40 Whatman ashless filter paper into a clean 100 ml volumetric flask. During filtering the inside of the beaker and the contents were rinsed with 6N HCl and triple distilled water and solution was made up to volume (100 ml) with triple distilled water. The solutions thus prepared were transferred into nalgene bottles for storage. The filter paper was saved for

acid insoluble determination, as described below.

Rock powder pellets were prepared for X-ray fluorescence as follows: roughly 2.5 g. of dry rock powder was weighed out into a plastic vial to which 3 drops of poly-vinyl-alcohol was added as a binding agent. Sample and binding agent were thoroughly mixed. The sample was then transferred to a 32 mm die, an additional 4 g. of borax was added as backing. This was compressed at (9 tons psi) pressure for 15 seconds (Turek and Riddle 1977).

Determination of Acid Insoluble

The filter paper containing the insoluble residue from acid dissolution was placed in a dry preweighed porcelain crucible and ignited in a Muffle furnace at about 950°C. After cooling it was reweighed. The difference in the two weighings is the weight of insoluble residue. A correction of 0.0001 g. was applied for the weight of the ashless paper. The acid insoluble content was calculated as follows:

$$\% \text{ Acid insoluble} = \frac{\text{Wt. of ash}}{\text{Wt. of sample}} \times 100$$

Determination of Loss on Ignition

For this measurement porcelain crucibles were deglassed to be of constant weight. The deglassed crucibles were dried at 110°C prior to use. Accurately 4 g. of rock powder was added to the preweighed crucible and reweighed. This gives weight of sample taken. The crucible was placed in a cold muffle furnace which was heated to 950°C for half an hour. This whole procedure takes about 5 hours. The crucibles were removed from the furnace, allowed to cool and reweighed. From this the loss on ignition was calculated as follows.

$$\% \text{ Loss on ignition} = \frac{\text{Wt. loss}}{\text{Wt. of sample}} \times 100$$

Where

Wt. loss = Weight of crucible and sample before ignition - Weight of crucible and sample after ignition.

Wt. of sample = Weight of crucible and sample before ignition - Weight of crucible.

In this measurement the samples were not dried, which means that the loss on ignition measurement also includes H_2O^- (humidity). However, this is a very small quantity which has been estimated as 0.3%. Furthermore, the obtained loss on ignition was not corrected for H_2O^- because it is constant and very small. The loss on ignition measurement is essentially a measure of $CO_2 + H_2O^+$. Most limestones and dolomites contain less than 1% H_2O^+ . This is a very useful measurement in that it allows a check on the CaO and MgO determinations.

Determination of CaO and MgO by Atomic Absorption Spectrometer

CaO and MgO were determined by atomic absorption spectrophotometer, using Varian Techtron model AA-5, on sample solutions prepared as described above.

Experimental. The operating conditions for the determination of CaO were:

Lamp current - 3 mA

Fuel - Acetylene + nitrous oxide support

Wave length - 422.7 nm

Slit - 100 μ

Reducing cone - 1 to 1.5 cm high

Optimum working range - 1 to 4 μ g/ml

Detection limit - 0.0005 μ g/ml

For MgO determination:

Lamp current - 3 mA

Fuel - Acetylene + air support

Wavelength - 285.2 nm

Slit - 100 u

Optimum working range - 0.1 to 0.4 ug/ml

Detection limit - 0.0003 ug/ml

The prepared solutions contained about 3,000 ug/ml Ca (corresponding to 30% CaO in sample) and 1000 ug/ml Mg (corresponding to 10% MgO in sample). Hence, dilution of samples was required for measurement at the most sensitive range as indicated above. Dilutions were made using an automatic dilutor; the required dilutions were made 10, 100, 500 or 2,500 depending on concentration.

Standards. A range of previously prepared standards containing known concentrations of Ca and Mg were used. For Ca the range of standards used was 1 to 5 ug/ml and for Mg the range of standards used was 0.01 to 1 ug/ml.

Calibration graphs of absorbance verses concentration were prepared and they were linear for the specified range of standards.

Calculations. Following calculations were made for CaO and MgO individually.

$$\% \text{ CaO or MgO} = \text{Concentration ug/ml} \times \frac{\text{Sa. vol.}}{\text{Sa. wt.}} \times F \times D \times 10^{-4}$$

Where

Concentration ug/ml = Concentration of Ca or Mg in solution

Sa. vol. = Original volume of sample -- 100 ml

Sa. wt. = Weight of the sample -- Ca 1 g.

F = Conversion factor from Ca to CaO 1.3992; and Mg to MgO 1.6579

D = Dilution factor

Determination of Al_2O_3 and SiO_2 by X-ray Fluorescence Method

Experimental. Al_2O_3 and SiO_2 were determined using a Phillips X-ray spectrometer model PW 1410/00/60. Primary X-ray source was from Phillips X-ray generator model PW 1140/N/60. Analysing conditions for Al and Si were as follows:

	Al	Si
Tube	Cr	Cr
Crystal	TLAP	TLAP
Collimator	Coarse 50 KV, 40 mA 150 LL, 170 W	Coarse 45 KV, 20 mA 140 LL, 220 W
Attenuation	3	3
FC	Volts 1710 (pot @ 540)	Volts 1590 (pot @ 500)
Count rate		
Peak angle	37.43°	31.78°
Standards	NBS 1 (1.2% Al_2O_3) NBS 88a (0.3% Al_2O_3)	USGS (42.15% SiO_2) NBS 1 (4.76% SiO_2)
Holder	Cu	Al
Peak count	100 seconds	100 seconds
Background count	40 seconds	40 seconds
Dead time corrections	- for Flow Counter is 0.000002 s./count	

Concentration of Al_2O_3 and SiO_2 was obtained by comparison of intensities with the intensities of standards. Background corrections and dead time corrections were made. Matrix corrections were not made, however, the

analyses were done against NBS standards which are carbonate rocks.

Dead time correction was made by using the following equation.

$$R_t = \frac{R_o}{1-R_T}$$

Where

R_t = True count rate

R_o = Observed counts

R_T = Constant delay (2×10^{-6} s.)

Results

The chemical analyses are given in Table 4. In addition to the determinations of CaO, MgO, Al_2O_3 , SiO_2 , LOI and acid insoluble (for 6N HCl) a calculated value for loss on ignition is given. The purpose of this is to check the CaO and MgO values. As LOI is essentially a measurement of CO_2 content and CO_2 is contained in $CaCO_3$ (44% CO_2) and $CaMg(CO_3)_2$ (56% CO_2). Therefore, the calculated LOI should be similar to the experimental LOI except that it will be lower as H_2O^+ (about 1%-1%) and H_2O^- (about 0.3%) are not accounted for. Generally the agreement between experimental and calculated LOI is very good. Where the agreement is poor it is likely that Ca and Mg may be in other than carbonate form (e.g. presence of gypsum).

TABLE 4
CHEMICAL ANALYSES

Sample No.	CaO	MgO	Al ₂ O ₃	SiO ₂	LOI	Calculated LOI	Acid insoluble
45.1	43.00	3.46	.34	6.46	40.17	37.44	13.08
45.2	36.17	4.08	2.54	25.00	31.57	32.79	28.08
45.3	36.18	3.47	.41	28.00	32.14	32.13	27.59
45.4	30.07	4.07	1.65	40.00	23.70	23.96	47.00
45.5	32.77	3.88	1.12	32.00	29.50	29.91	33.64
45.6	10.54	3.36	3.81	75.46	8.72	11.92	80.24
45.7	47.28	1.13	1.07	5.87	40.16	38.23	11.00
45.8	32.80	1.25	.35	37.00	28.15	27.03	38.03
45.9	17.25	2.26	1.03	64.27	14.17	15.97	69.01
45.10	24.16	2.00	.55	55.00	18.93	21.10	57.78
45.11	43.11	1.63	1.51	6.40	33.22	35.52	11.55
45.12	48.45	1.60	1.56	8.85	38.23	39.45	14.28
45.13	46.61	2.22	2.02	10.09	37.56	38.91	17.09
45.14	43.07	1.61	2.30	7.75	38.20	35.47	14.87
45.15	44.80	.56	.58	20.00	35.31	35.66	20.25
45.16	47.35	.40	.21	4.47	40.93	37.49	5.87
45.17	53.44	1.73	2.23	1.39	38.66	43.71	13.61
45.18	15.53	3.23	2.68	38.20	24.98	15.70	72.10
45.19	43.11	2.54	2.04	17.00	35.01	36.52	21.58
45.20	31.93	1.74	.36	38.00	27.72	26.89	37.63
78.1	27.62	22.70	.16	.40	47.20	46.60	3.25
78.2	32.72	20.45	.12	.44	46.99	48.11	2.36
78.3	35.29	20.37	.24	.58	46.98	50.03	2.51
78.4	34.41	20.45	.10	.47	45.79	49.43	2.84
78.5	31.05	21.91	.24	.64	46.69	48.40	2.95
78.6	30.02	22.97	.27	1.38	46.04	48.77	3.31
78.7	29.24	21.27	1.08	1.81	45.61	46.29	7.63
78.8	31.03	21.65	.74	1.49	45.72	48.11	6.18
78.9	32.11	19.36	.48	1.01	45.98	46.43	3.23
78.10	30.21	21.88	.69	1.85	45.11	47.71	6.67
78.11	31.09	20.61	.40	.86	45.05	47.01	7.96
78.12	24.14	22.47	.89	2.53	44.85	43.61	4.55
78.13	34.50	20.50	.68	1.33	46.09	49.56	5.14
78.14	30.96	20.05	.46	1.33	45.90	46.29	5.78
78.15	30.19	21.06	.64	1.19	46.08	46.80	5.96
78.16	29.65	21.80	.27	.62	47.04	47.20	4.36
78.17	30.15	21.03	.32	.70	47.13	46.74	5.01
78.18	31.87	21.06	.23	.55	47.03	48.17	5.42
78.19	32.76	20.49	.39	.86	46.83	48.18	5.60
78.20	31.07	21.35	.30	.91	46.62	47.81	6.50

TABLE 4 continued

CHEMICAL ANALYSES							
Sample No.	CaO	MgO	Al ₂ O ₃	SiO ₂	LOI	Calculated LOI	Acid insoluble
80.1	46.45	4.26	.35	3.52	41.58	41.03	6.05
80.2	41.39	4.10	.37	10.80	38.92	36.89	11.83
80.3	51.00	2.80	.33	3.14	42.07	42.98	5.08
80.4	49.97	4.01	.32	2.54	42.41	43.51	4.58
80.5	49.90	4.13	.57	2.97	41.74	43.58	5.84
80.6	48.25	3.05	.46	4.51	41.20	41.10	7.13
80.7	49.88	3.46	.42	4.41	40.98	42.83	7.87
80.8	48.23	3.35	.21	3.54	42.16	41.41	5.43
80.9	51.70	3.15	.34	3.44	42.31	43.91	5.39
80.10	50.86	3.35	.53	3.73	42.01	43.47	6.11
100.1	30.83	22.12	.20	.70	46.72	48.92	4.93
100.2	30.61	22.86	.18	.76	46.82	49.11	2.31
100.3	35.19	16.67	.24	.75	46.53	45.88	4.75
100.4	31.07	20.69	.27	.71	46.20	47.08	2.69
100.5	29.30	20.54	.24	.81	46.58	45.53	4.21
100.6	30.21	19.02	2.83	10.54	39.09	44.57	16.12
100.7	25.89	16.36	2.08	10.52	36.46	38.24	22.43
100.8	28.23	16.32	1.09	10.60	37.36	39.98	20.44
100.9	34.50	13.90	4.45	7.80	37.13	40.96	14.15
100.10	29.27	14.93	1.99	7.99	37.68	39.33	18.24
100.11	30.98	12.70	1.88	8.91	37.42	38.22	20.20
100.12	32.80	12.55	1.91	8.09	39.26	39.47	17.26
100.13	30.99	12.54	.44	20.14	37.96	38.04	19.16
100.14	27.62	13.66	1.22	10.37	37.93	36.64	20.07
100.15	31.06	16.36	3.76	7.36	39.21	42.31	16.97
100.16	36.17	15.30	.66	1.95	43.28	44.14	6.03
100.17	30.10	18.14	1.38	2.55	43.59	43.52	8.48
100.18	37.92	10.82	.48	1.38	41.35	41.58	4.90
100.19	43.12	8.21	.58	1.81	39.81	42.77	6.71
100.20	30.95	19.76	1.00	2.18	43.64	45.96	7.21
59.1	44.83	1.02	.36	15.00	38.03	36.14	14.63
59.2	50.03	1.22	.14	1.66	42.88	40.48	4.77
59.3	51.02	1.33	.25	2.88	42.01	41.38	4.70
59.4	43.06	.96	.27	22.00	33.57	34.74	24.14
59.5	43.06	.86	.27	25.00	32.82	34.63	26.07
59.6	48.33	1.27	.27	5.60	40.78	39.20	8.12
59.7	37.91	.82	.79	33.00	27.16	30.56	32.16
59.8	51.79	.80	.13	5.66	39.24	41.40	11.68
59.9	48.26	1.37	.43	5.85	39.68	39.26	11.02
59.10	36.21	.96	.45	27.44	31.31	29.38	30.73

TABLE 4 continued

CHEMICAL ANALYSES

Sample No.	CaO	MgO	Al ₂ O ₃	SiO ₂	LOI	Calculated LOI	Acid insoluble
6.1	31.05	21.26	.72	2.62	44.24	47.69	6.12
6.2	30.20	17.58	1.48	4.62	41.55	41.24	13.29
6.3	30.18	16.96	1.88	2.15	41.00	42.28	15.27
6.4	25.87	15.93	3.16	16.00	39.08	37.77	19.41
6.5	27.60	18.20	1.22	5.20	42.68	41.62	11.48
6.6	29.29	12.45	2.50	9.82	37.39	36.61	20.84
6.7	25.90	16.70	2.93	7.61	39.05	38.64	17.40
6.8	27.58	15.13	2.79	9.20	37.66	38.23	21.34
6.9	25.85	16.03	2.38	7.53	37.90	37.86	19.22
6.10	24.09	16.51	2.30	10.95	39.11	37.02	19.54
6.11	26.71	21.44	.23	.99	46.54	44.50	6.00
6.12	27.53	19.36	2.01	5.19	43.10	42.85	12.08
6.13	27.56	20.41	1.23	5.91	43.52	44.03	11.72
6.14	26.72	21.04	.58	1.76	45.80	44.06	7.02
6.15	32.77	21.45	.49	2.73	45.10	49.95	4.52
6.16	24.12	23.06	.21	.82	46.87	44.25	1.63
6.17	32.77	19.41	.74	2.27	44.36	47.01	10.22
6.18	27.62	18.60	.87	2.63	43.81	42.08	11.04
6.19	25.83	20.20	.77	2.66	45.15	42.45	8.82
6.20	30.11	20.18	.41	2.15	45.87	45.77	6.68
62.1	42.06	4.13	.64	7.29	37.51	37.45	16.36
62.2	37.77	4.06	2.57	10.45	34.57	34.02	24.20
62.3	34.42	7.09	5.10	35.00	27.95	34.73	38.71
62.4	31.93	5.91	1.18	30.00	30.40	31.48	32.02
62.5	41.42	3.35	.41	22.00	33.38	36.09	24.73
62.6	36.19	4.18	1.37	25.00	32.29	32.91	27.62
62.7	38.00	3.51	.97	24.08	34.50	33.59	22.73
62.8	36.95	5.23	1.27	20.84	33.64	34.66	24.21
62.9	37.59	1.22	.51	38.00	24.03	30.44	44.14
62.10	9.69	3.38	1.49	75.00	9.08	11.30	77.27
62.11	36.99	3.38	1.41	6.14	36.05	32.66	17.47
62.12	34.33	.92	1.27	35.00	27.99	27.87	37.49
62.13	34.42	.92	.78	40.00	25.00	27.94	46.34
62.14	41.30	3.82	2.08	7.26	36.25	36.51	18.97
62.15	30.08	.48	.67	41.55	24.93	24.05	43.73

Classification by Rock Type

Rock samples were grouped into limestones and dolomite on the basis of calculated dolomite content based on the chemical analysis results as follows:

CaO and MgO converted to CaCO_3 and MgCO_3 as follows:

$$\% \text{CaO} \times 1.7848 = \% \text{CaCO}_3$$

$$\% \text{MgO} \times 2.0915 = \% \text{MgCO}_3$$

Then

$$\frac{\% \text{CaCO}_3}{\text{Mol.wt. (CaCO}_3)} = A, (\% \text{ At. units})$$

$$\frac{\% \text{MgCO}_3}{\text{Mol.wt. (MgCO}_3)} = B, (\% \text{ At. units})$$

Dolomite = $B \times \text{Mol.wt. of dolomite (184.35)}$ in wt. %

Calcite = $(A-B) \times \text{Mol.wt. of CaCO}_3$ in wt. %

Further, the rocks have been divided into two subgroups on the basis of the alumina content.

Frequency distribution diagrams were plotted for the dolomite and alumina contents of the rocks in order to determine whether the distribution of the above components is unimodal or bimodal (Figs. 2 and 3).

From Fig. 2 it is evident that the distribution is bimodal. The break between limestones and dolomites is 20-70% dolomite. In this study for the purpose of classification the break between limestones and dolomites has been taken as 45% dolomite content. Therefore, 0-45% dolomite content is called a limestone and >45% dolomite content it is called a dolomite.

Harvey et al. (1974) have grouped 122 carbonate rocks into dolomites and limestones on the basis of dolomite content by taking 50% dolomite content as the criterion for the division. This is in agreement with the 45% value used in this study.

Pettijohn (1975) classified carbonate rocks on the basis of the dolomite content as follows:

Dolomitic limestone	- 10-50% dolomite
Calcite dolomite	- 50-90% dolomite
Dolomite	- 90-100% dolomite

Blatt et al. (1972) pointed out that the term dolomite refers both to the mineral species $\text{CaMg}(\text{CO}_3)_2$ as well as to a rock, their definition of dolomite as a rock is based on dolomite content $< 50\%$ of dolomite.

The grouping of rocks into limestone and dolomite as used in this study is therefore in agreement with Pettijohn (1975) and Blatt et al. (1972). Moreover, there are no standard rules reported in the literature for subdivision of carbonate rocks on the basis of chemical or mineralogical compositions.

Another classification of carbonate rocks into two categories has been done on the basis of Al_2O_3 content (Rogers 1976). Fig. 3 shows the frequency distribution. The histogram is slightly bimodal. The apparent break is between 1.5% to 2% Al_2O_3 , and the rocks can be divided into low alumina ($< 1.75\%$ Al_2O_3) and higher alumina ($> 1.75\%$ Al_2O_3) rocks. Out of 92⁺ rocks 17 fall into high alumina rocks and 75 fall into low alumina rocks. The above groupings were made for the purpose of statistical analysis.

+ Of the 121 rocks used 92 are the same as investigated by Garber.

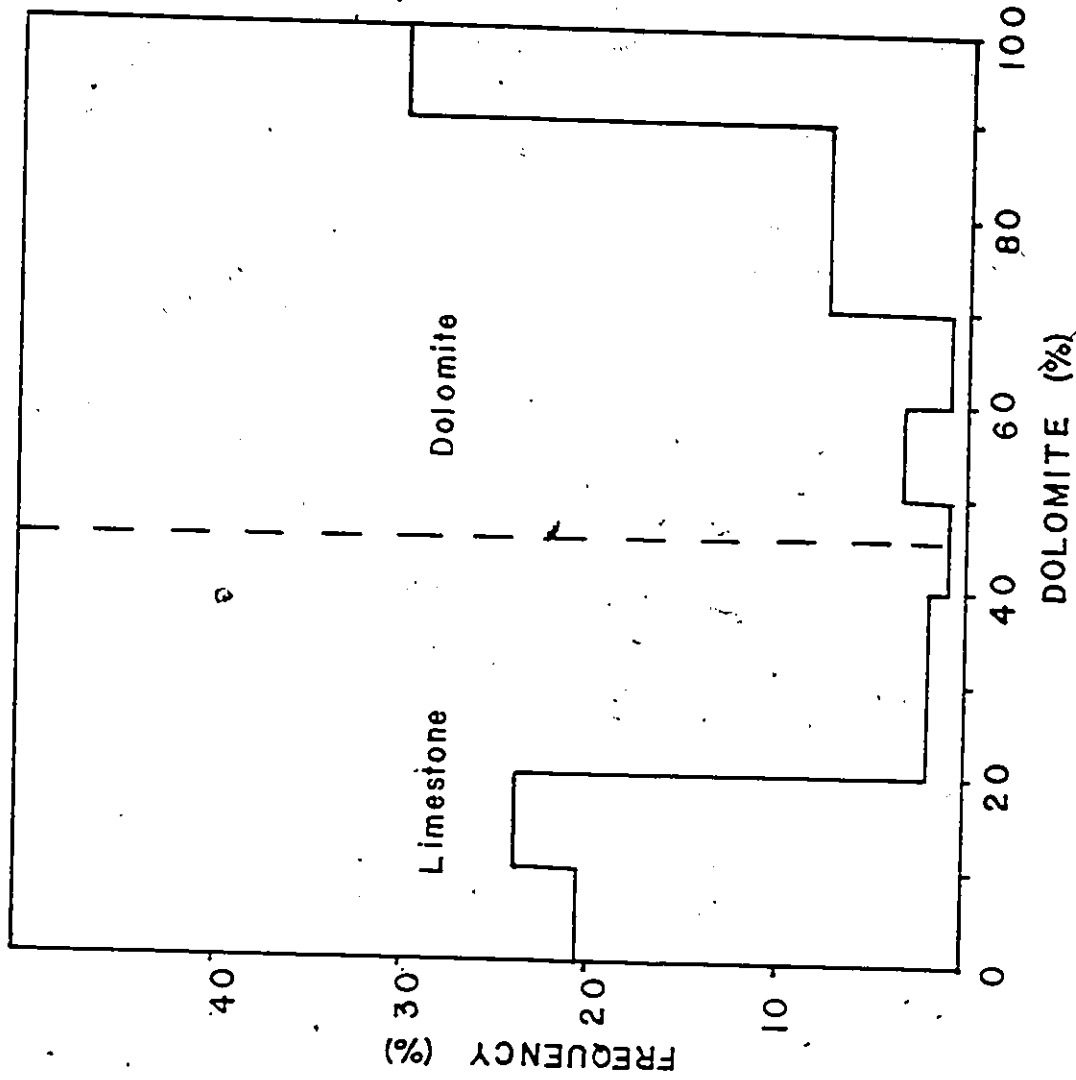


Fig 2 Limestone - dolomite frequency distribution

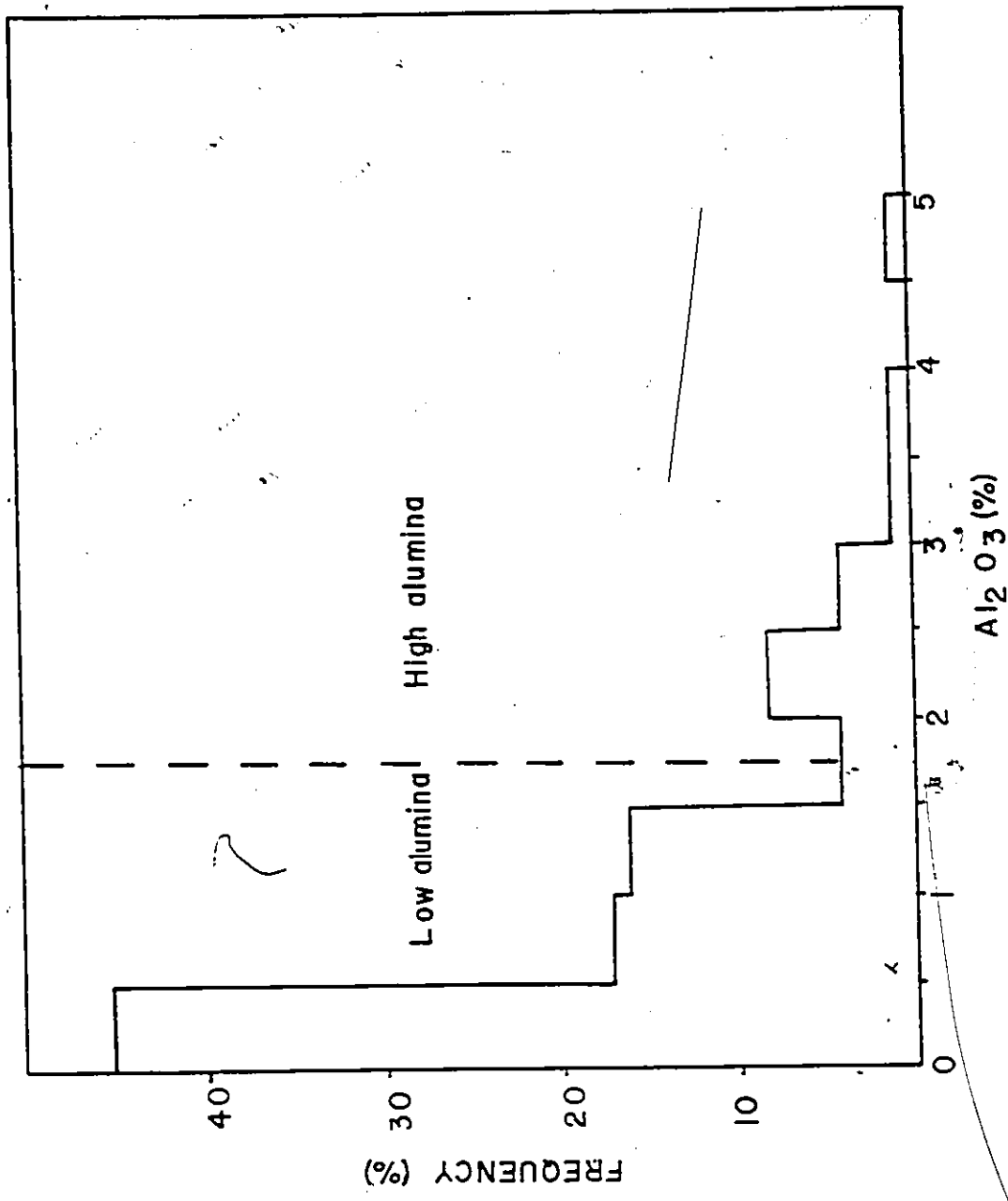


Fig 3 Al₂O₃ frequency distribution

CHAPTER 5

STATISTICAL ANALYSIS OF CHEMICAL AND ADSORPTION DATA

Statistical Treatment and Computation of Data

Statistical evaluation of analytical data has been done using linear regression and correlation. The slope of the line of best fit, the intercept and the correlation coefficient can be tested for significance at different levels of probability. An IBM 360/70 computer was used for the statistical evaluation of data as well as to plot the individual data points. For linear regression the BMD-02 (Biomedical Computer Program 1973) correlation with transgeneration program was used. This program computes simple correlation coefficients, averages, and measures of dispersion of variables or transgenerated variables. All data were statistically analysed as well as selected data groups on combined variables such as CaO and MgO or Al₂O₃ and SiO₂.

The results of the BMD-02 program gave linear plots, however, it was apparent from these plots that not all the relations were linear and some of them may be a log-normal or log-log functions. For this purpose SAS (Statistical Analysis System 1976) programs were used. Most of the relations derived were to log-log functions (Figs 7-31). The equation for the line of best fit is:

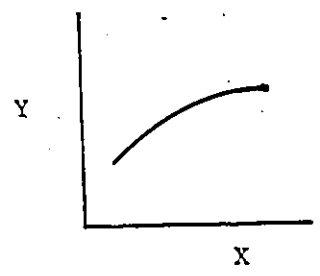
$$\ln Y = b \ln X + \ln C$$

or

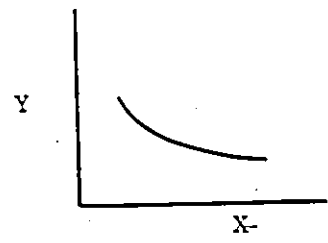
$$Y = C X^b$$

If $Y = 1 X^b$ and $b = 1$ or close to 1, and when plotted a linear relationship will be obtained.

If $b = 0.5$ or less a direct non linear relationship similar to the following is obtained. As X increases the increase in Y will be progressively lesser.



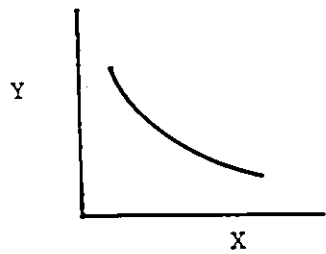
If $b = -0.5$ or less an inverse non linear relationship is obtained. As X increases the decrease in Y is progressively lesser.



When $b = 1.5$ and above a direct non linear relationship is obtained, and as X increases the increase in Y is progressively greater.



When $b = -1.5$ an inverse non linear relationship similar to the following is obtained. As X increases the decrease in Y is progressively greater.



For comparison figure 4 was obtained to linear relation and also to log-log relation. In both the cases the computed correlation coefficient (r)

was the same. In both the cases the observed relationship was direct and linear.

As described earlier, the samples were grouped into dolomites, limestones, high and low alumina rocks representing 47, 45, 17 and 78 cases respectively, to check if these groups represented populations of themselves and if they did then the correlations within these groups will be higher than correlations of the samples as a whole. Separate statistical analyses were done for dolomites and limestones and also low and high alumina rocks. Plots of dolomites and limestones were analysed and interpreted. Since majority of the carbonate rocks fall into low alumina group separate discussion of high and low alumina groups was not made. Table 5 is the regression and correlation analyses of between different combinations of the variables: water, Cu, Pb and Zn sorption, CaO, MgO, Al₂O₃, LOI and acid insoluble.

TABLE 5

Regression Analysis of Dolomites and Limestones Combined

Fig No	Variable Y	Variable X	Sample size	r	Slope b	Intercept	Correlation significant at 5% level	Correlation significant at 1% level
4	Calculated LOI	Determined LOI	92	.969	.9623	2.26	Yes	Yes
5	SiO ₂	Acid insoluble	92	.981	1.0028	-4.34	Yes	Yes
6	Acid insoluble	Al ₂ O ₃ + SiO ₂	92	.986	.954	3.89	Yes	Yes
Regression Analysis of Dolomites								
7	ln MgO	ln CaO	47	.493	-2.05	9.91	Yes	Yes
10	ln MgO	ln Al ₂ O ₃	47	.666	-0.10	2.90	Yes	Yes
8	ln CaO	ln Al ₂ O ₃	47	.365	-0.036	3.38	Yes	No
12	ln CaO + MgO	ln Al ₂ O ₃	47	.741	-0.063	3.87	Yes	Yes
14	ln Al ₂ O ₃	ln SiO ₂	47	.875	.76	-1.05	Yes	Yes
	ln Cu	ln H ₂ O	47	.751	.34	5.07	Yes	Yes
	ln Pb	ln H ₂ O	47	.361	.159	5.86	Yes	No
	ln Zn	ln H ₂ O	47	.447	.168	4.06	Yes	Yes
16	ln H ₂ O	ln CaO	47	.356	-2.52	5.79	Yes	No

TABLE 5 Continued

Fig No	Variable Y	Variable X	Sample size	r	Slope b	Intercept	Correlation significant at 5% level	Correlation significant at 1% level
20	ln Cu	ln CaO	47	.01	.024	3.98	No	No
24	ln Pb	ln CaO	47	.287	1.05	1.84	No	No
25	ln Zn	ln CaO	47	.171	.48	1.90	No	No
17	ln H ₂ O	ln MgO	46	.628	-4.01	9.16	Yes	Yes
22	ln Cu	ln MgO	46	.531	-1.524	8.61	Yes	Yes
28	ln Pb	ln MgO	46	.512	-1.661	10.38	Yes	Yes
29	ln Zn	ln MgO	46	.584	-1.385	7.67	Yes	Yes
19	ln H ₂ O	ln Al ₂ O ₃	47	.899	.786	-2.34	Yes	Yes
23	ln Cu	ln Al ₂ O ₃	47	.682	.26	4.22	Yes	Yes
30	ln Pb	ln Al ₂ O ₃	47	.396	.17	5.54	Yes	Yes
31	ln Zn	ln Al ₂ O ₃	47	.443	.15	3.65	Yes	Yes

Regression Analysis of Limestones

7	ln MgO	ln CaO	45	.199	-0.991	4.53	No	No
11	ln MgO	ln Al ₂ O ₃	45	.376	.303	9.934	Yes	Yes
9	ln CaO	ln Al ₂ O ₃	45	.440	-0.179	3.59	Yes	Yes
13	ln CaO + MgO	ln Al ₂ O ₃	45	.403	-0.14	3.68	Yes	Yes

TABLE 5 Continued

Fig No	Variable Y	Variable X	Sample size	r	Slope b	Intercept	Correlation significant at 5% level	Correlation significant at 1% level
15	ln Al ₂ O ₃	ln SiO ₂	45	.426	.356	-1.20	Yes	Yes
	ln Cu	ln H ₂ O	45	.489	.104	4.77	Yes	Yes
	ln Pb	ln H ₂ O	45	.195	-0.034	5.84	No	No
	ln Zn	ln H ₂ O	45	.133	-0.021	4.10	No	No
16	ln H ₂ O	ln CaO	42	.678	-6.713	22.92	Yes	Yes
20	ln Cu	ln CaO	42	.237	-0.523	6.45	No	No
24	ln Pb	ln CaO	42	.346	.086	5.66	Yes	No
25	ln Zn	ln CaO	42	.091	-0.140	4.70	No	No
18	ln H ₂ O	ln MgO	45	.454	.91	2.93	Yes	Yes
21	ln Cu	ln MgO	45	.471	.20	4.34	Yes	Yes
26	ln Pb	ln MgO	45	.017	-0.0009	5.98	No	No
27	ln Zn	ln MgO	45	.203	.06	4.21	No	No
19	ln H ₂ O	ln Al ₂ O ₃	45	.759	1.34	-1.67	Yes	Yes
23	ln Cu	ln Al ₂ O ₃	45	.542	.204	4.58	Yes	Yes
30	ln Pb	ln Al ₂ O ₃	45	0.000	.003	5.98	No	No
31	ln Zn	ln Al ₂ O ₃	45	.037	.01	4.16	No	No

CHAPTER 6

DISCUSSION OF RESULTS

The following discussion is based on the chemical compositional relationship of dolomites and limestones, and includes: the comparative study between calculated loss on ignition and determined loss on ignition, SiO_2 and acid insoluble, acid insoluble and Al_2O_3 plus SiO_2 , MgO and CaO , MgO and Al_2O_3 , CaO and Al_2O_3 , MgO plus CaO and Al_2O_3 , Al_2O_3 and SiO_2 .

Water and metal sorption against CaO , MgO , and Al_2O_3 for dolomites and limestones were also studied and will be discussed below.

Chemical Composition of Carbonates

Calculated LOI vs Determined LOI

Theoretical loss on ignition was calculated for the samples to check the experimentally determined loss on ignition.

$$\begin{array}{l} \text{CaO} \times 0.7825 \text{ (factor)} = \text{CO}_2 \\ \text{MgO} \times 1.101 \text{ (factor)} = \text{CO}_2 \end{array} \quad \left. \vphantom{\begin{array}{l} \text{CaO} \\ \text{MgO} \end{array}} \right\} = \text{Calculated LOI}$$

The maximum allowable difference between determined and calculated loss on ignition is 3% (Turek personal communication). The linear plot obtained for the data of calculated LOI and determined LOI showed good correlation (Fig 4). A calculated difference of 2.24% exists between the calculated LOI and determined LOI, therefore, this value is within the maximum allowable difference of 3%.

SiO_2 vs Acid Insoluble

A linear plot (Fig 5) for SiO_2 and acid insoluble content shows a

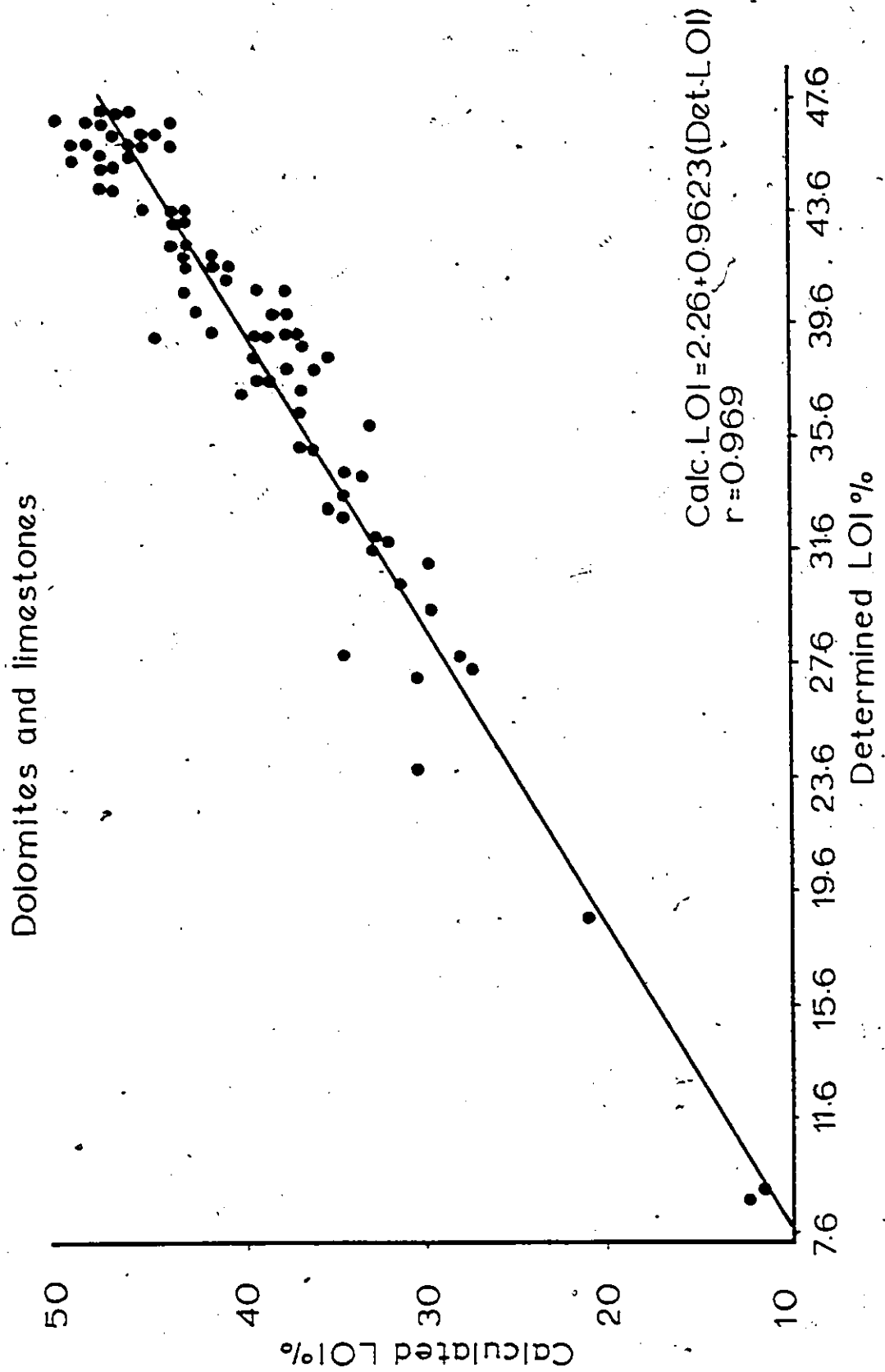


Fig 4 A plot of calculated LOI vs determined LOI

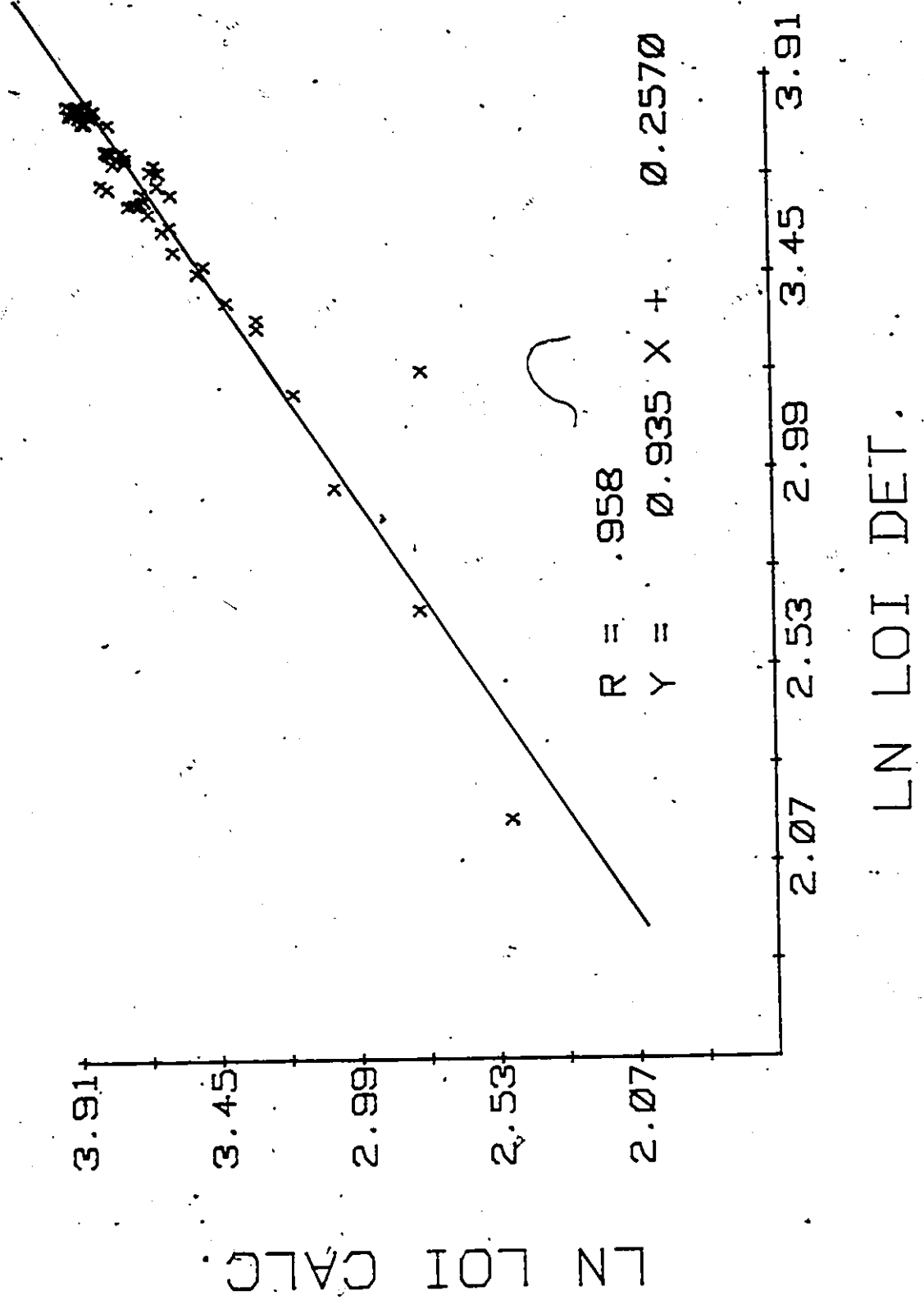


Fig 4 A plot of calculated LOI vs determined LOI

Dolomites and limestones

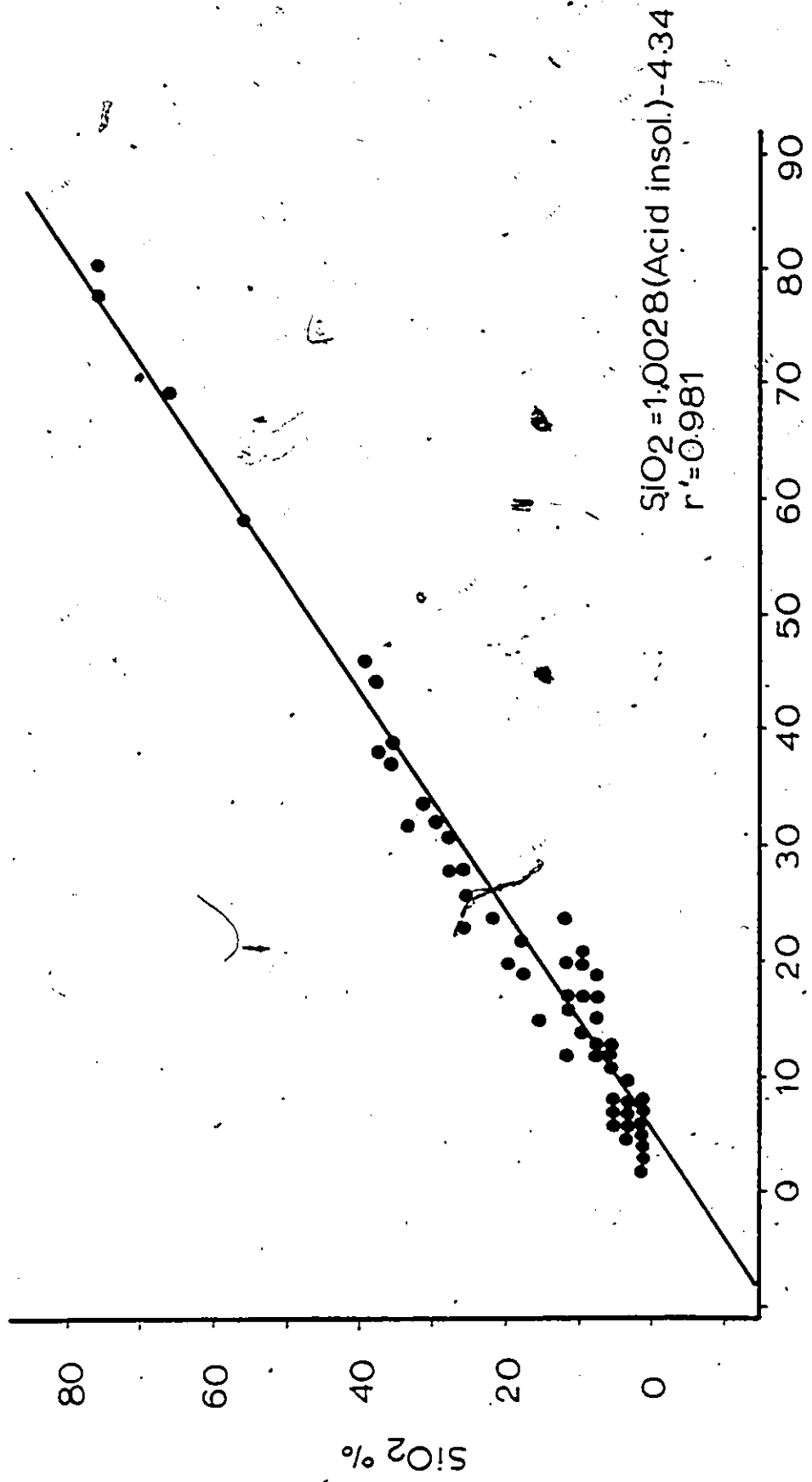


Fig 5 A plot of SiO₂ content vs acid insoluble content

direct correlation. This is to be expected since the acid insoluble reflects the content of clay minerals, chalcedony, free quartz and glauconite. Many carbonate rocks contain these as accessories.

Acid Insoluble vs $Al_2O_3 + SiO_2$

A direct correlation exists between acid insoluble and the combined Al_2O_3 and SiO_2 (Fig 6). This relationship is related to the undigested clay and also silica content and accounts for bulk of the acid insoluble. Clays are largely insoluble. The slight solubility of clay minerals in acid varies with the nature of acid, the acid concentration, the acid-to-clay ratio, the temperature and the duration of treatment. Also the solubility of the various clay mineral groups is different (Nutting 1943, Pask and Davis 1945, Grim 1968). Since most of the clay is insoluble the undigested clay shows a direct correlation with the acid insoluble content. In the above section a direct correlation between SiO_2 and acid insoluble was observed ($r=.981$). Infact the combined $Al_2O_3+SiO_2$ gives a marginally better correlation coefficient ($r=.986$). The added alumina content due to clay improves the relationship.

MgO vs CaO

An inverse relationship exists between MgO and CaO contents of dolomites. This is expected inverse relationship. The MgO and CaO contents of limestones show no significant correlation; however, the line of best fit indicates similar but weak inverse relation (Fig 7). Statistical analysis indicated that not all the relations were linear and some of them may be a log-normal or log-log functions, therefore figures 7 to 31 were computed on log - log relationship.

Error analysis has been done on the slopes of limestones and dolomites which indicated that the slopes are statistically same but their intercepts

Dolomites and limestones

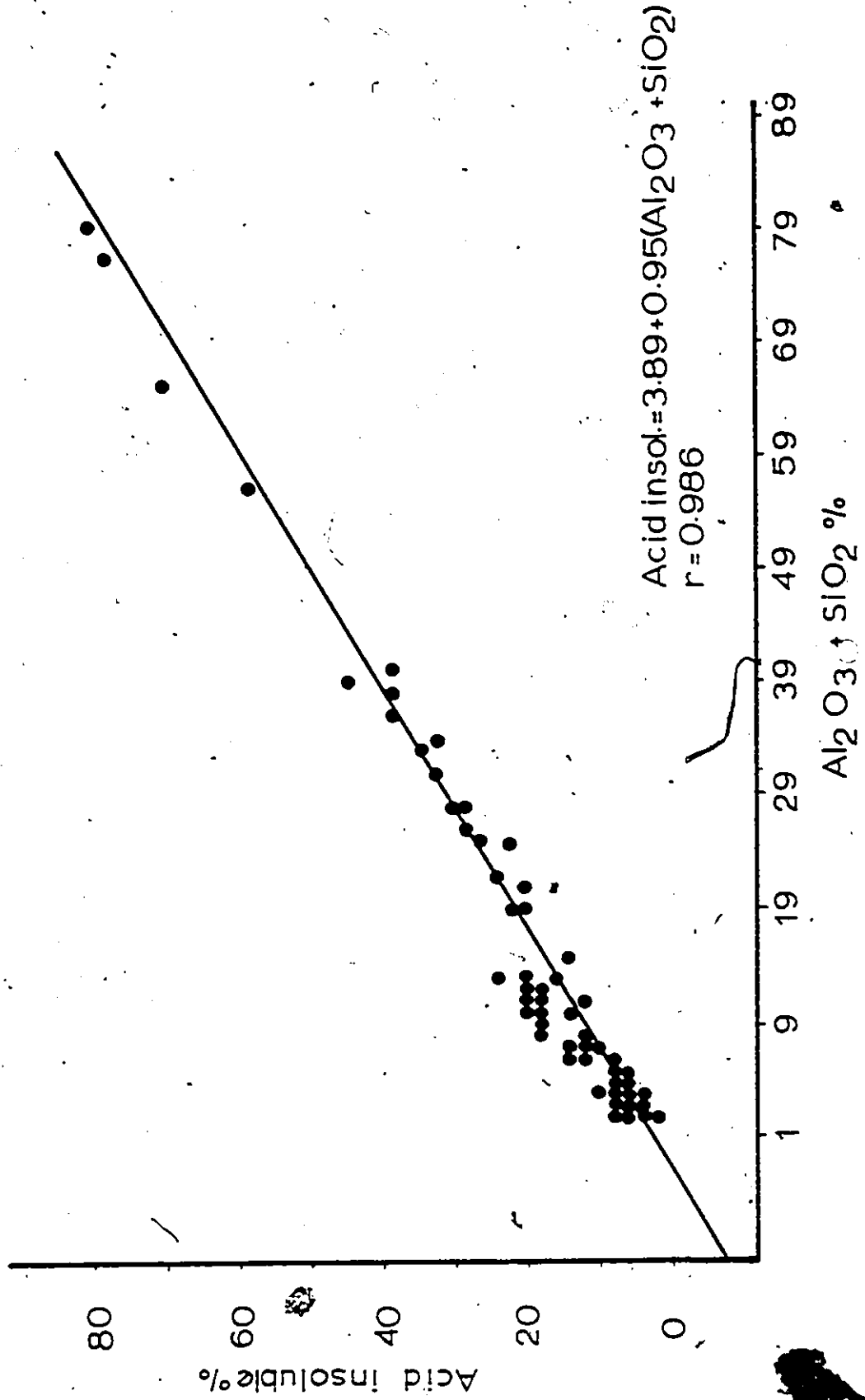


Fig 6 A plot of acid insoluble content vs combined Al₂O₃ and SiO₂ content

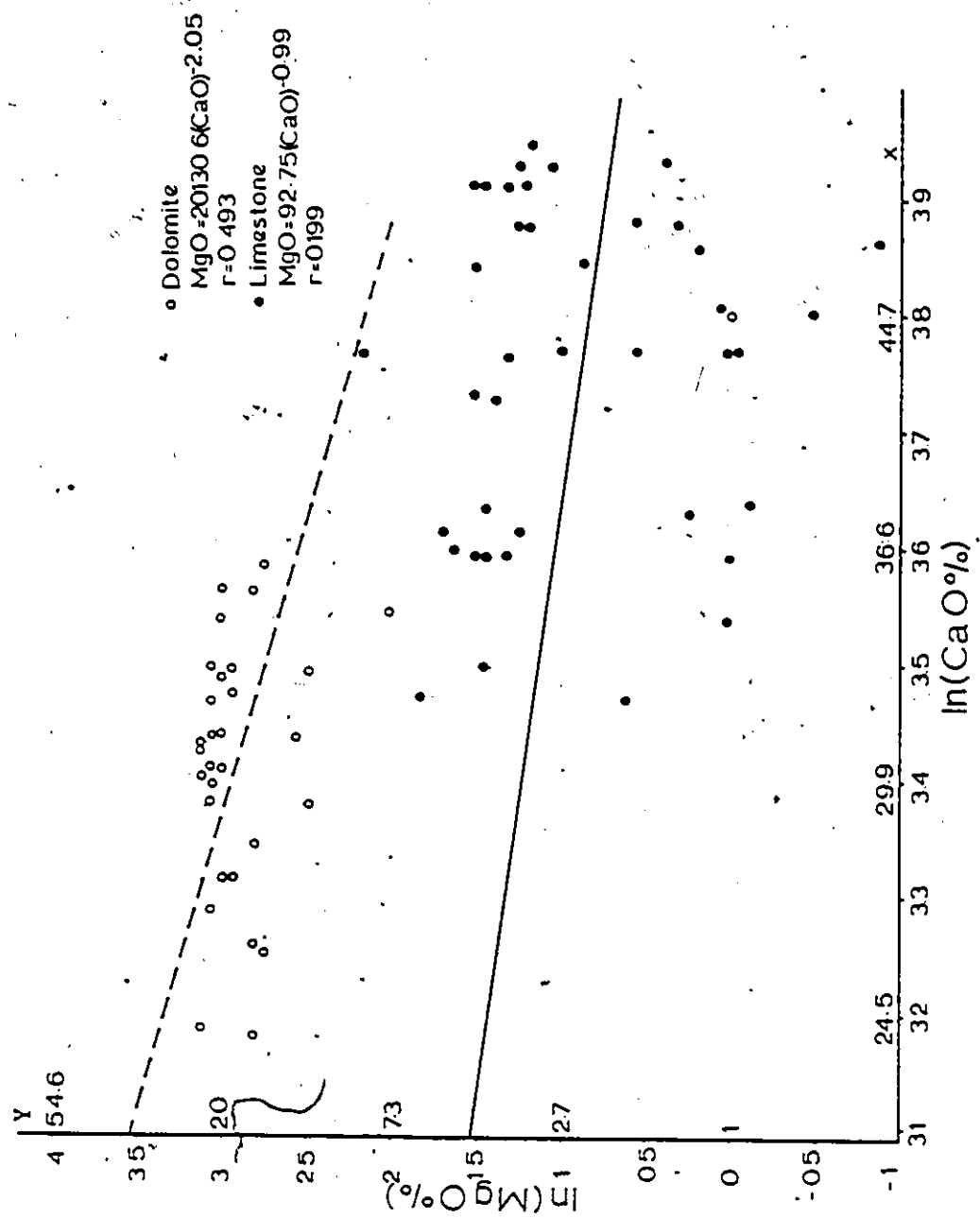


Fig 7 A plot of MgO content vs CaO content for carbonate rocks

are statistically different, and the relationships are also statistically different.

Increase in CaO content decreases the MgO content. This relationship is in accordance with the mineralogical composition governing the two carbonate rock types. The chemical composition of limestones reflects closely their mineral composition. Because limestones are primarily composed of calcite the content of CaO is high. If Mg content in limestones exceeds by 1% or 2%, this indicates the presence of mineral dolomite (Pettijohn 1975).

Dolomites give a much better correlation than the limestones. The probable cause for scatter of points observed in limestones is due to calcite which is able to take varying proportions of Mg ion into solid solution. Minor substitutions of Mg ion occurs in calcite, but the tendency to form the ordered phase dolomite is very great (Berry and Mason 1959).

CaO vs Al₂O₃

In both the rock types, an inverse relationship between CaO and Al₂O₃ contents was observed (Figs 8 and 9). This is because the Al₂O₃ content is directly related to clay mineral content. Illite and less often kaolinite are the most common clays in the carbonate rocks (Grim et al. 1973, Ostram 1959, Weaver 1958). If there is an increase in the clay accessories there would be a decrease of calcite or dolomite content of the carbonate rocks. Hence the above relation is expected.

Relative scatter of points is greater in dolomites rather than in limestones due to low calcite content in essentially a magnesium rich rock. CaCO₃ and MgCO₃ form a solid solution series (Garrels and Mackenzie 1971) in dolomite, and the variability of Ca in solid solution causes the scatter of points.

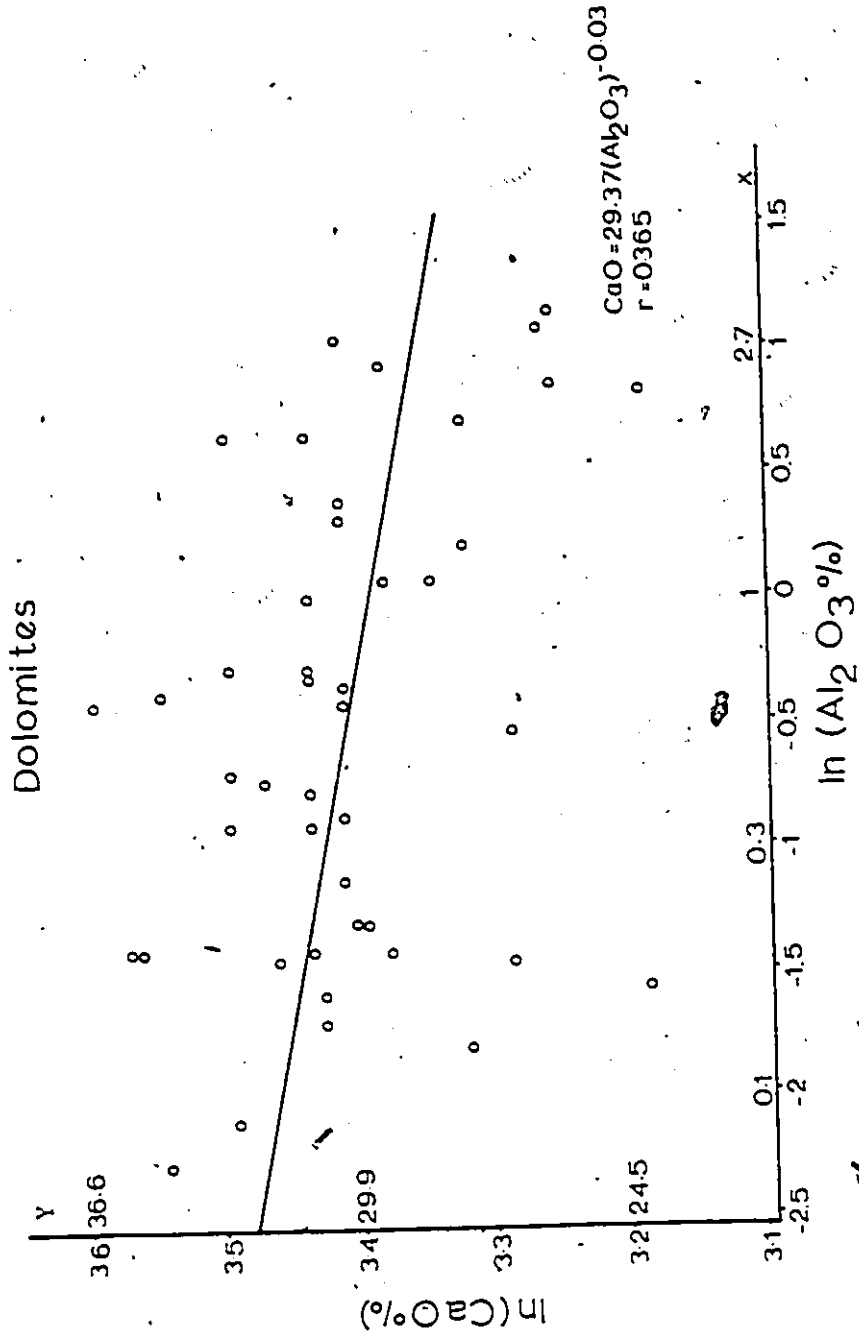


Fig 8 A plot of CaO content vs Al₂O₃ content for dolomites

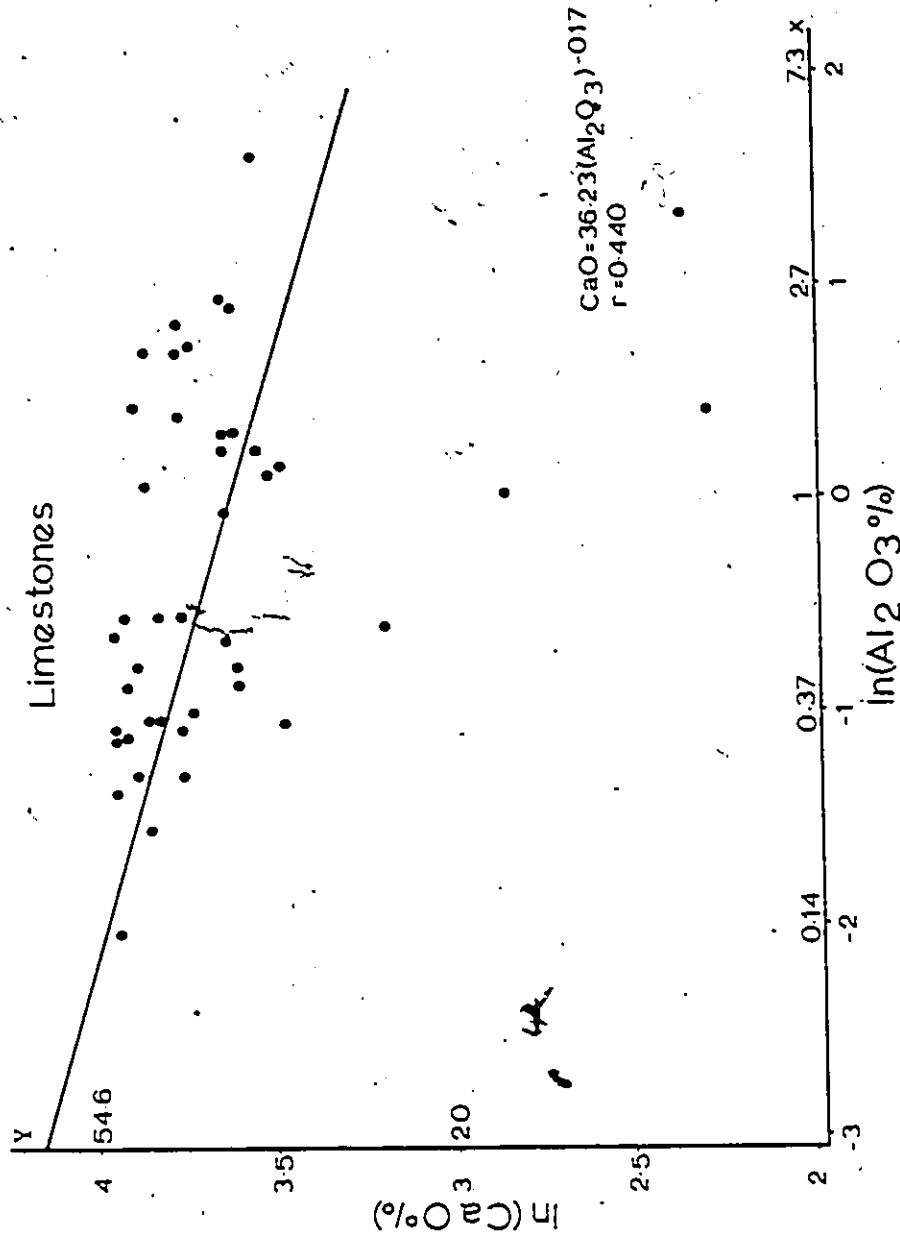


Fig 9 A plot of CaO content vs Al₂O₃ content for limestones

MgO vs Al₂O₃

It was observed that in dolomites Al₂O₃ content decreases with increase in MgO content (Fig 10). This indicates simply that clay in dolomite replaces mineral dolomite in the rock so if one increases the other has to decrease.

A direct correlation exists between MgO and Al₂O₃ contents of limestones (Fig 11) which is somewhat unexpected in view of previous trends shown above. It is possible that the Mg in limestones is clay associated (Mg⁺⁺) occurs as a commonest exchangeable cation on the clay surface, Grim 1968). This possibility is ruled out, however, since there is too little alumina. The average content of Al₂O₃ and MgO of limestones used in this work is 1.03% and 2.66% respectively. This amount of Al₂O₃ has to support 2.66% of MgO and this is not possible. Other possibility is that the high alumina limestones tend to be more dolomitized, in other words the clay itself promotes the dolomitization process so the higher the clay content of the limestones the higher the dolomitized portion within the limestone (Hudec personal communication). Sonnenfeld (1964) reviewed dolomitization and stated that magnesium bearing solutions lose their magnesium compounds within a short distance on contact with bentonites. He further states that " if this unloading of magnesium occurs over montmorillonite and other magnesium rich clays, then there is no reason to believe that such magnesium carrying waters would not react with limestones if brought in contact with them over a sufficient period of time ".

Potts (1959, cf. Keller, 1963) immersed clay (mainly montmorillonite) suspensions in sea-water for 36 and 86 hours. His data shows a marked increase of 195% in the amount of exchangeable Mg ions.

Carroll and Starkey (1960) have observed a similar relation. They immersed samples of montmorillonite, illite and kaolinite in sea-water for

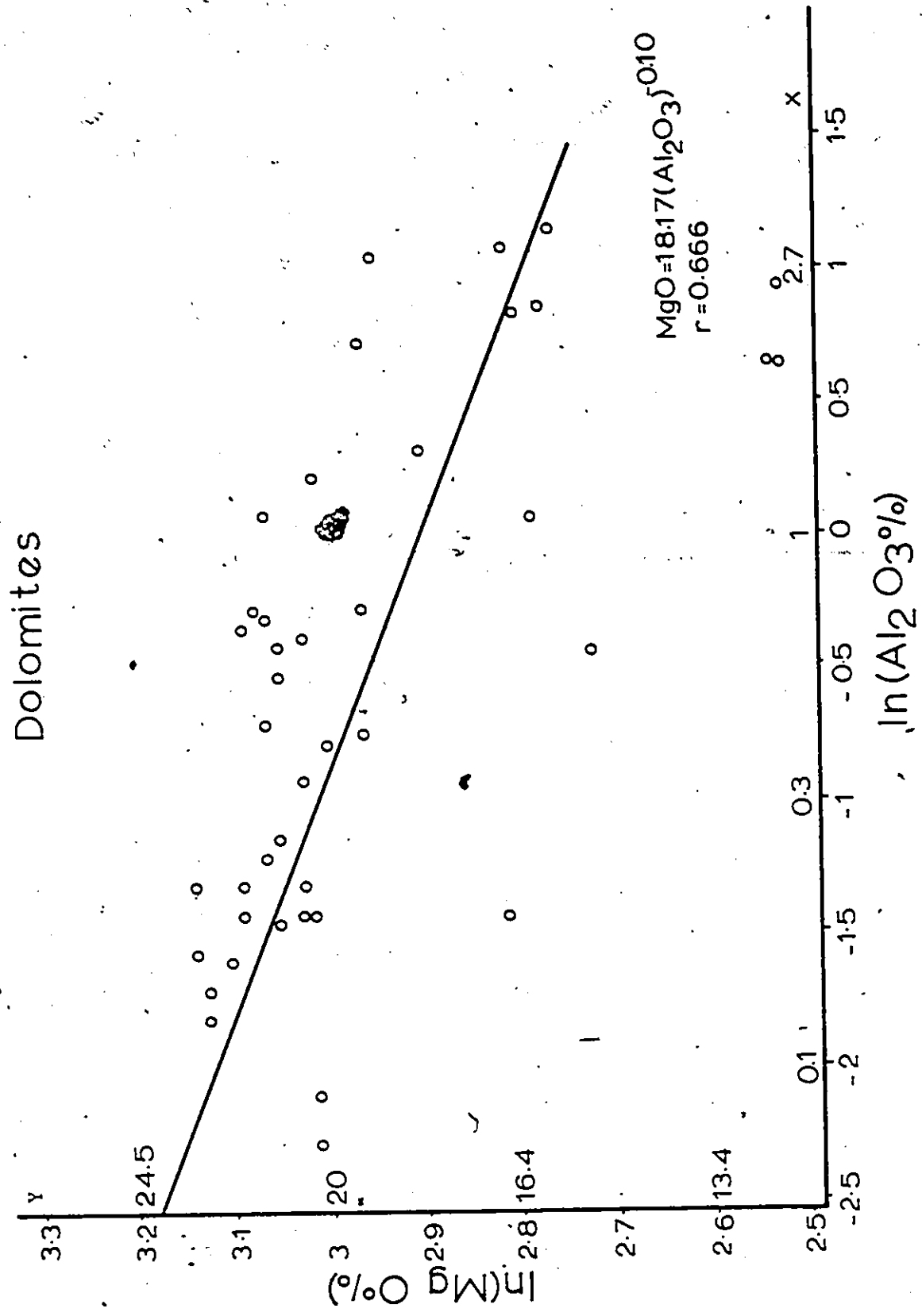


Fig 10 A plot of MgO content vs Al₂O₃ content for dolomites

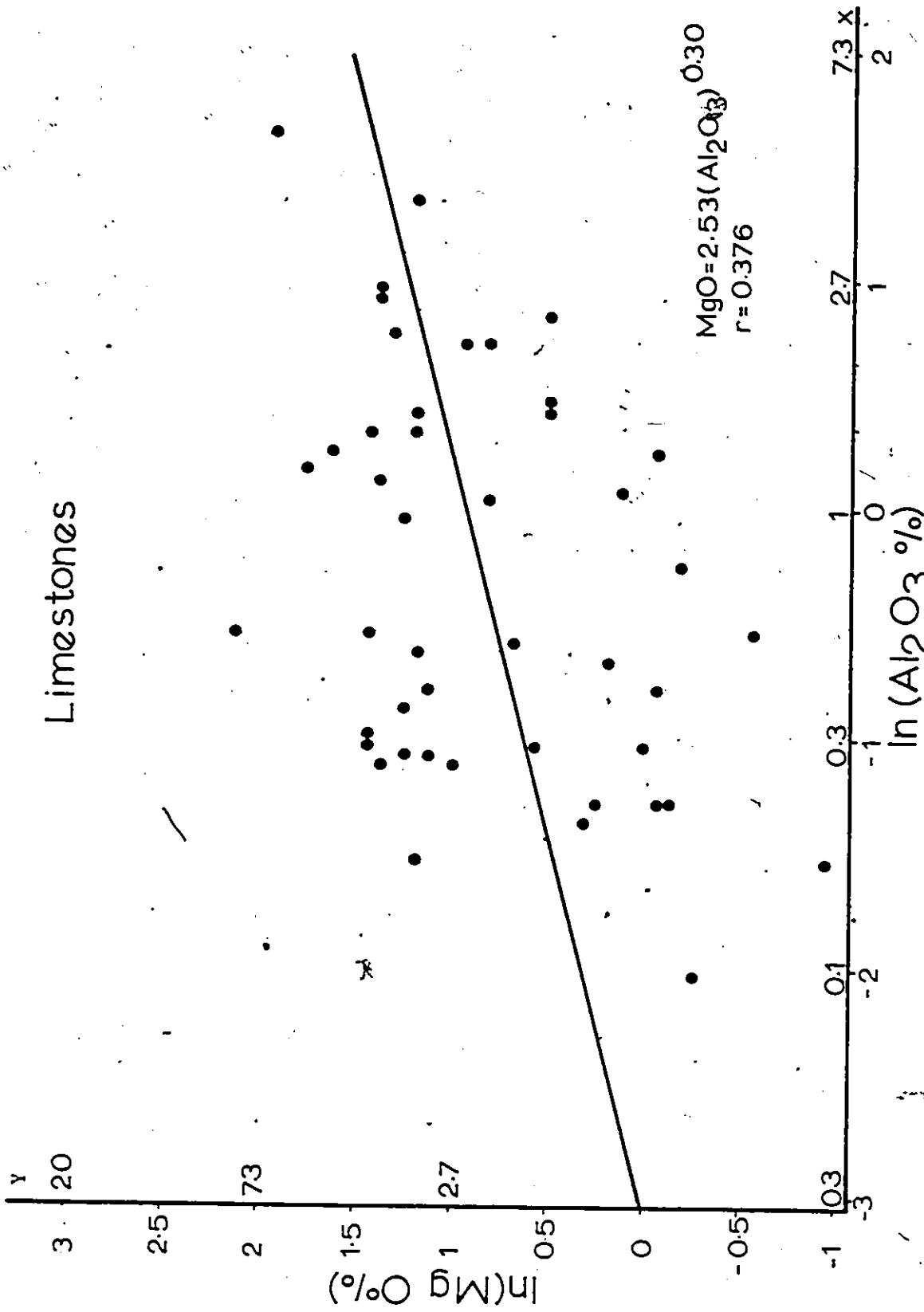


Fig 11 A plot of MgO content vs Al_2O_3 content for Limestones

10 and 150 days. They have found a marked increase in the amount of exchangeable Mg ions from a given solution. Presence of clay minerals in limestones may have considerable role in the process of dolomitization by taking the Mg ions and rendering them on to calcite to promote dolomitization

$$(Mg^{++} + 2 \cdot CaCO_3 = CaMg (CO_3)_2 + Ca^{++}).$$

There is a better correlation between MgO and Al_2O_3 in dolomites rather than in limestones. The probable cause for scatter of points observed in limestones is due to calcite which is able to take varying proportions of Mg ion in solid solution.

Total Carbonate Content vs Al_2O_3

Total carbonate content (combined MgO and CaO) shows an inverse relationship with Al_2O_3 content of both the limestones and dolomites (Figs 12 and 13). The Al_2O_3 content is related to clay minerals and as expected increase in clay content would displace the carbonate content of the dolomites and limestones, and therefore an inverse relation is seen between the carbonates and Al_2O_3 contents.

Al_2O_3 vs SiO_2

A direct relationship was observed between Al_2O_3 and SiO_2 contents of both the carbonate rock types (Figs 14 and 15). There is much better correlation in dolomites than in limestones ($r = 0.875$ and 0.714 for dolomites and limestones respectively). This is probably due to the presence of free quartz and to a degree different type of clays.

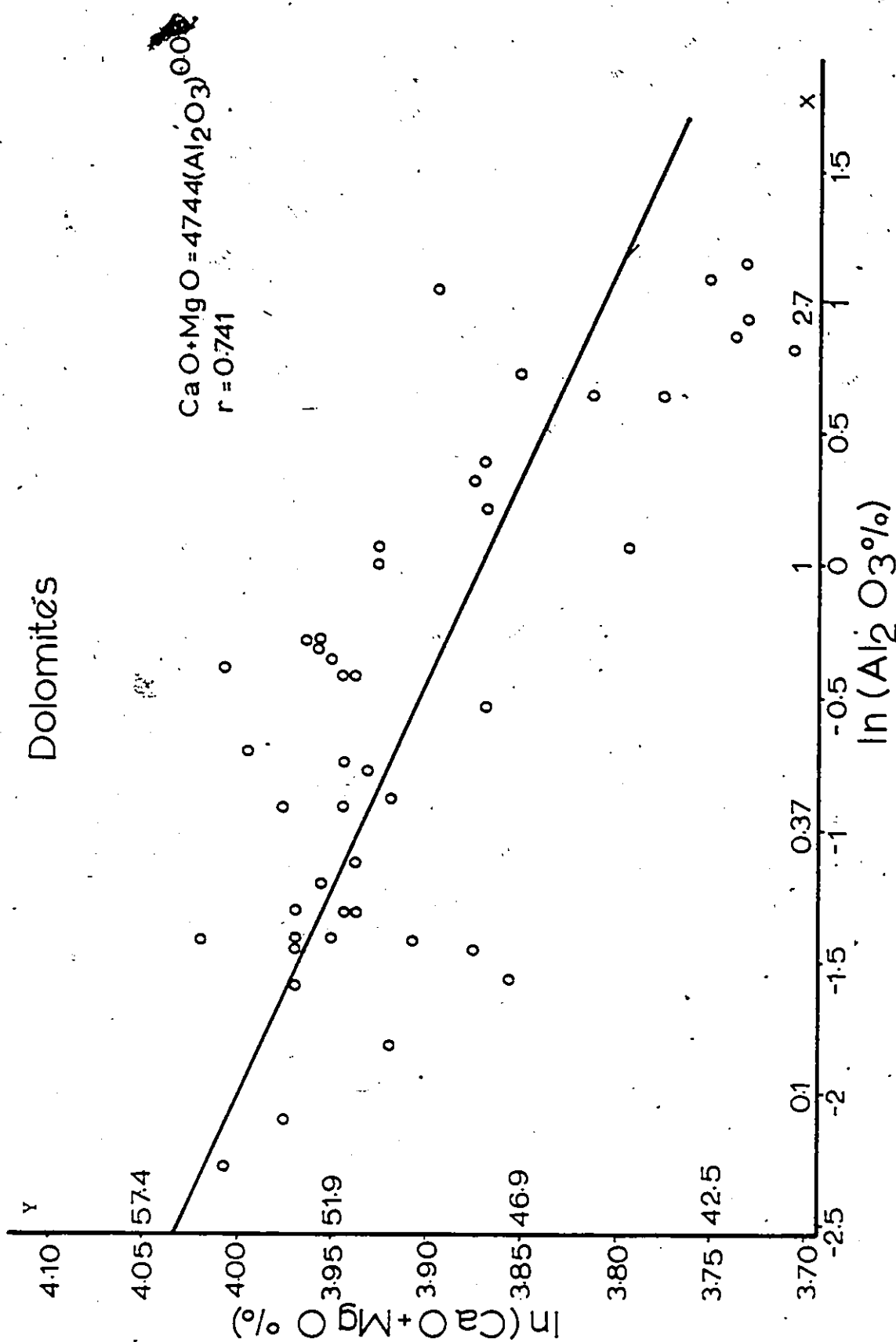


Fig 12 A plot of total carbonate content vs Al₂O₃ content for dolomites

Limestones

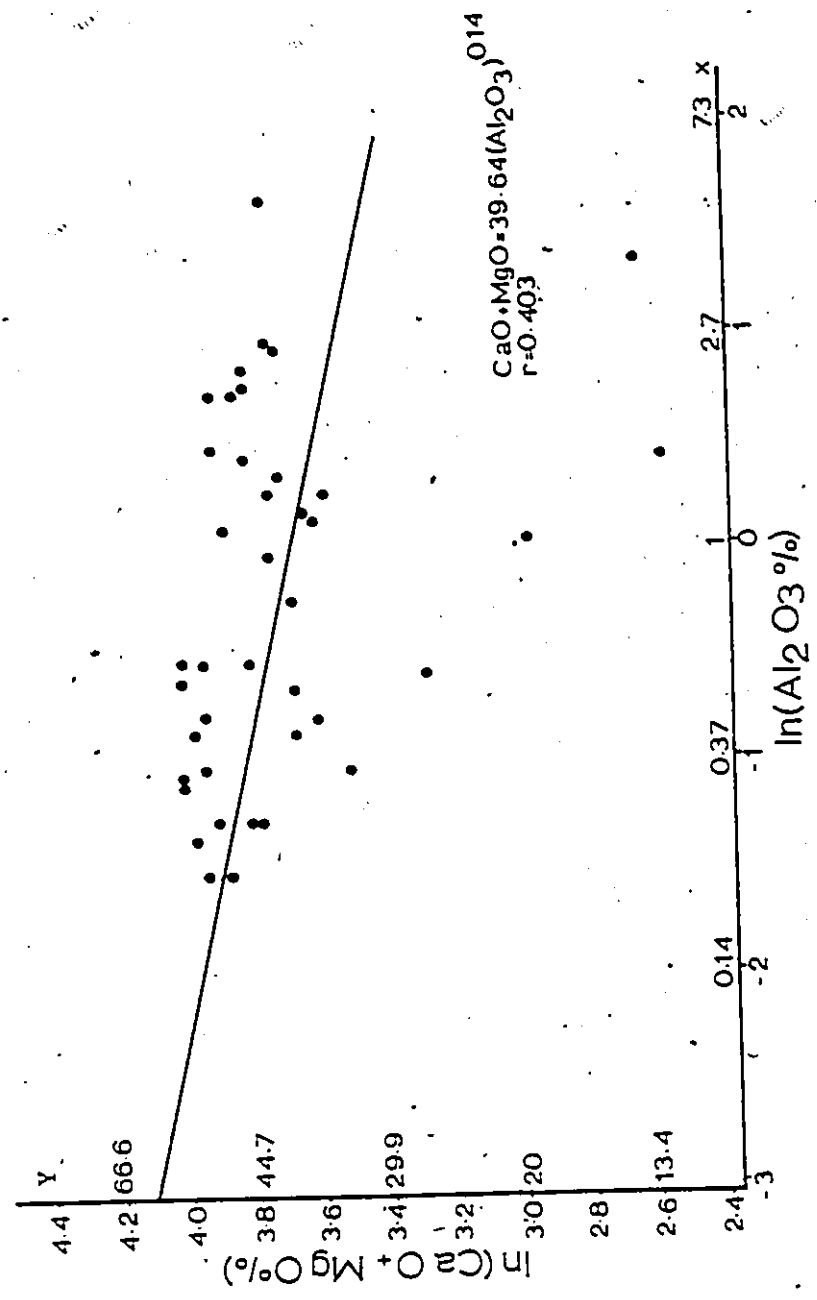


Fig 13 A plot of total carbonate content vs Al₂O₃ content for limestones

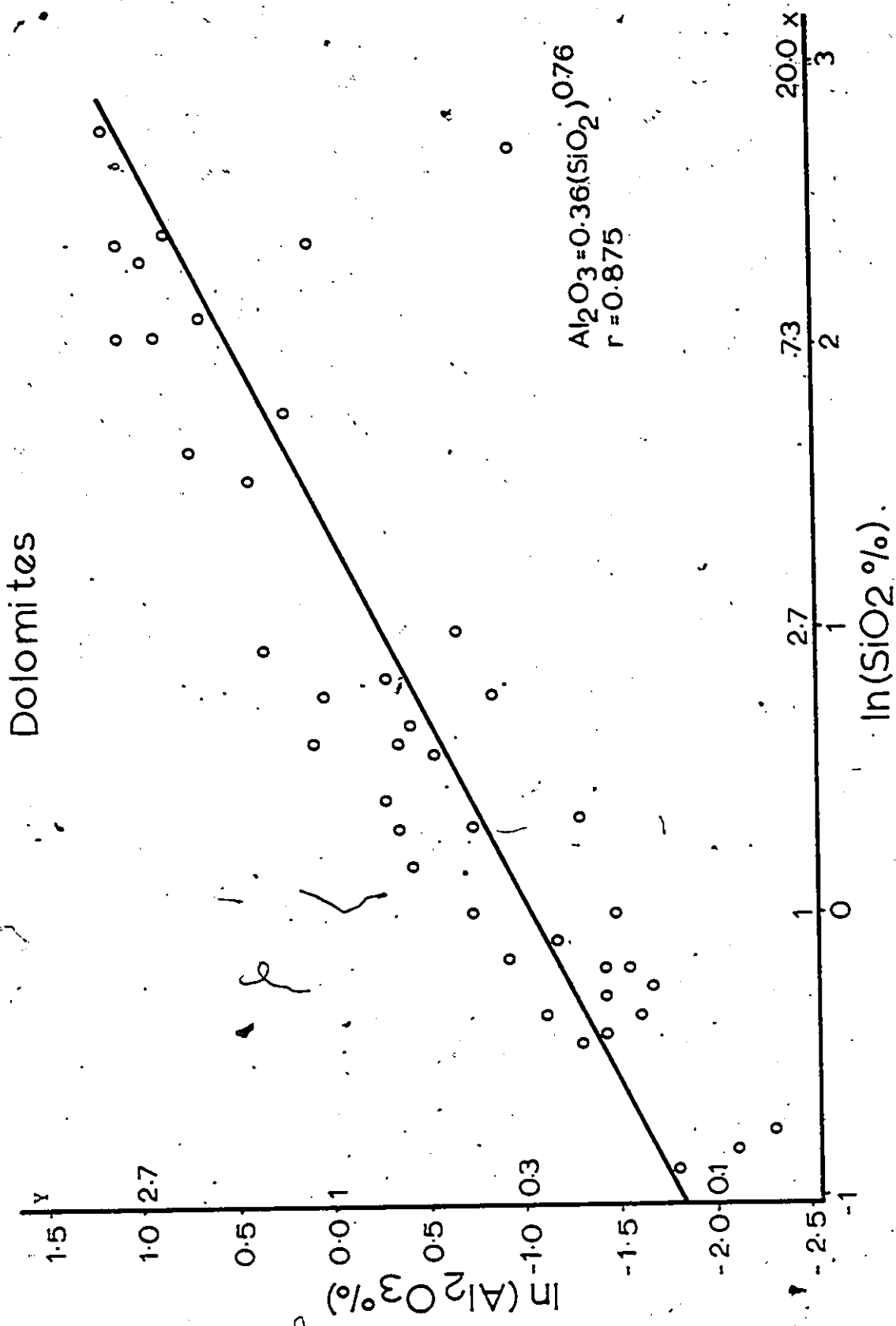


Fig 14: A plot of Al₂O₃ content vs SiO₂ content for dolomites

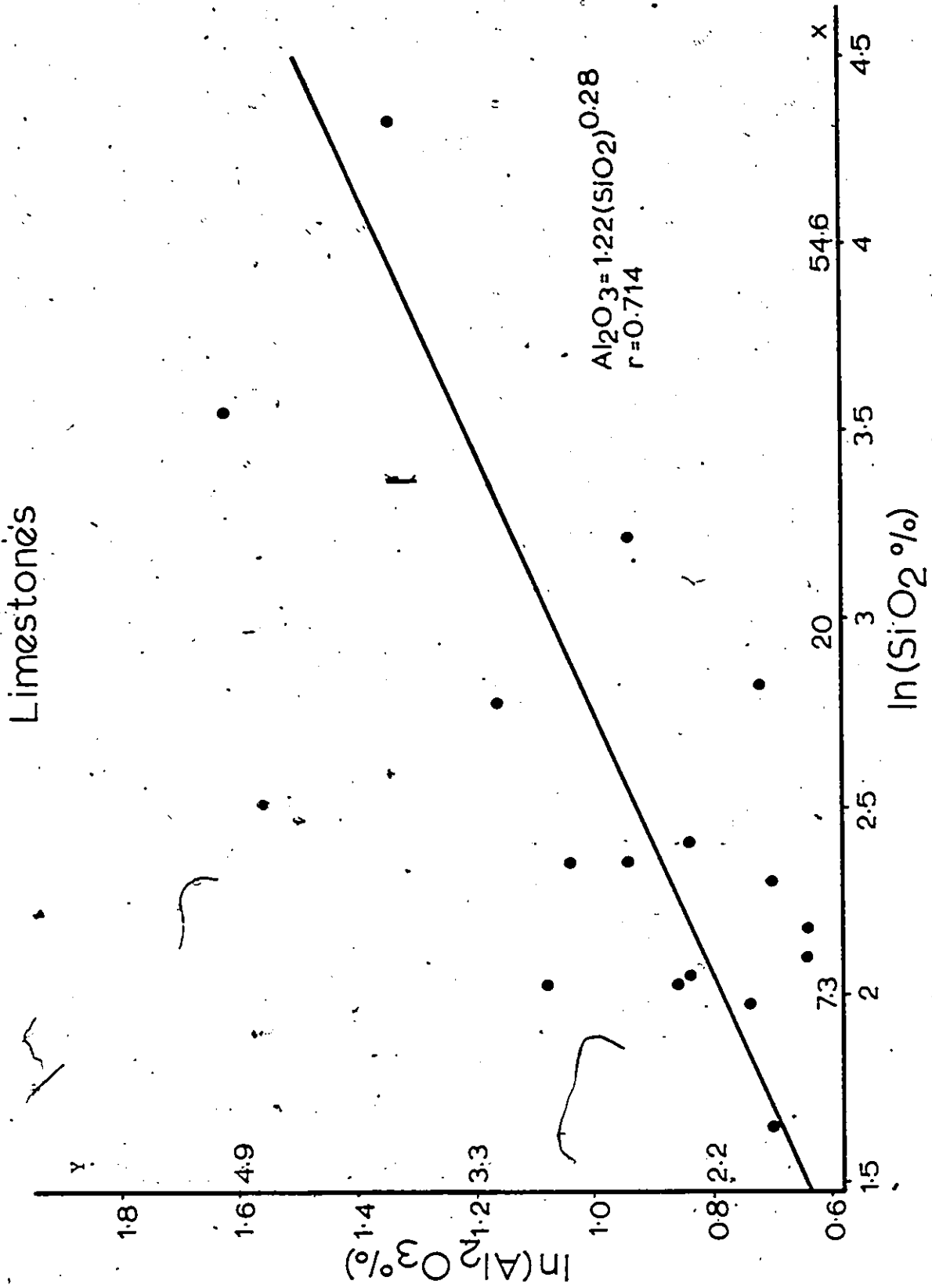


Fig 15 A plot of Al_2O_3 content vs SiO_2 content for limestones

Water Sorption

H₂O vs CaO

It was observed that water sorption decreases with increase in CaO content for both the carbonate rock types (Fig 16). As shown earlier, clay content decreases with increase in the CaO content. It was indicated in chapter 2 that the clays possess greater surface area than calcite and dolomite. Water sorption is a direct function of surface area. It is therefore expected that the decrease in the clay content would decrease the total available surface area in the carbonate rocks for water sorption.

H₂O vs MgO

Inverse relation exists between water sorption and MgO content of dolomites (Fig 17). Same explanation can be applied as was to H₂O verses CaO relationship.

There is a direct relationship between water sorption and MgO content of limestones (Fig 18). Since it was already shown in figure 11 that a direct relationship exists between alumina and magnesium contents in limestones it is not surprising that a direct relationship should also exist between water sorption and magnesium content of limestones, as magnesium is clay related.

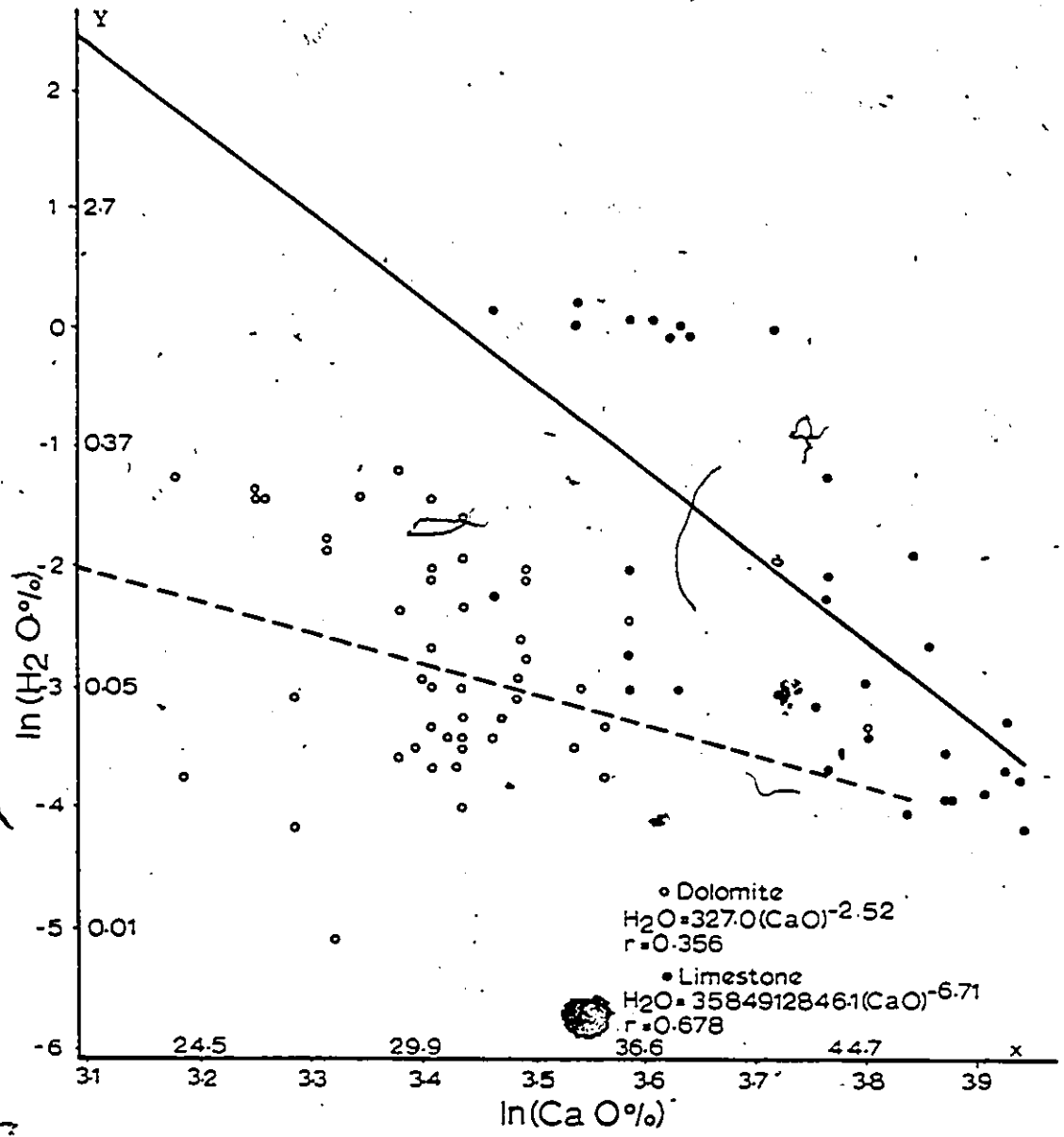


Fig 16 A plot of adsorbed water (%) at 45% R.H vs CaO content for carbonate rocks

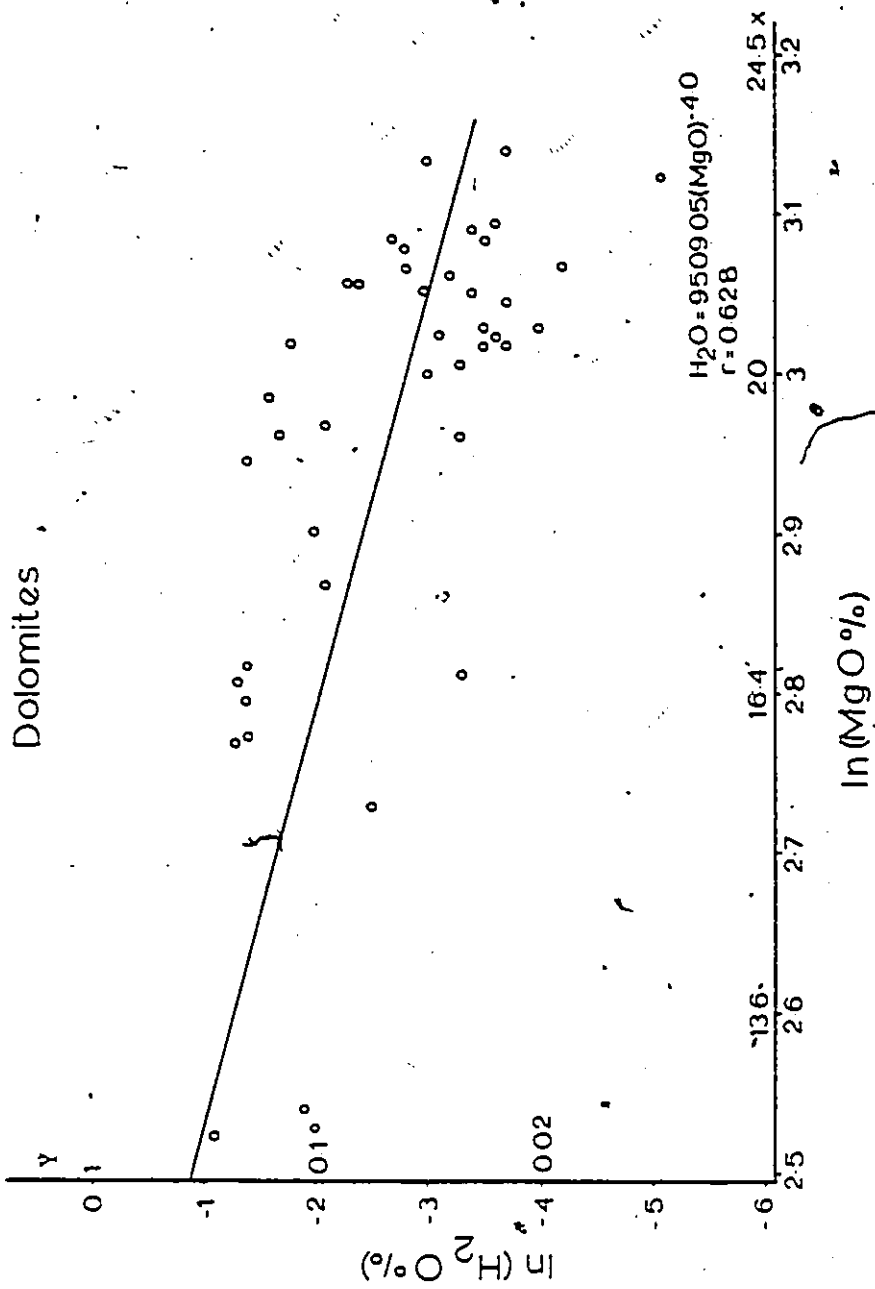


Fig 17 A plot of adsorbed water (%) at 45% R.H vs MgO content for dolomites

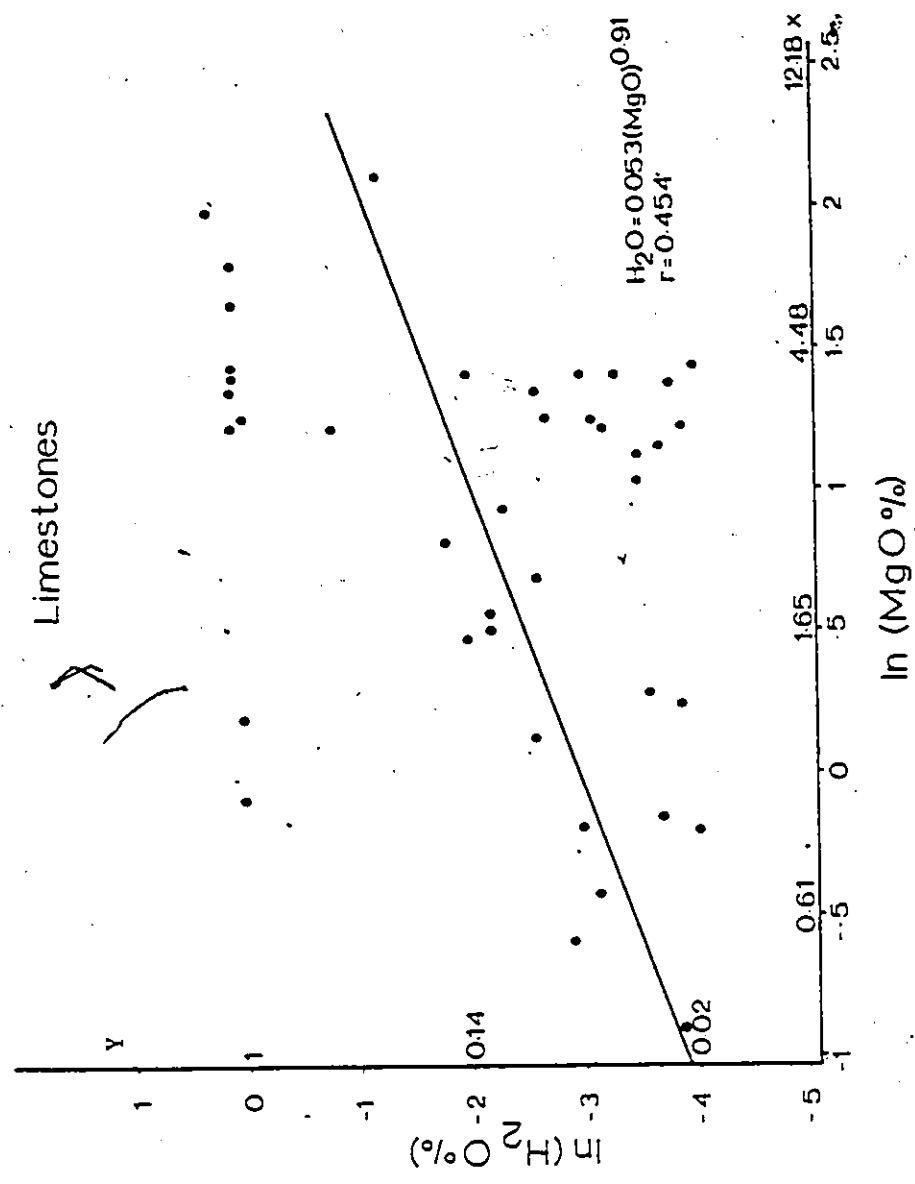


Fig 18 A plot of adsorbed water (%) at 45% R.H vs MgO content for limestones

H₂O vs Al₂O₃

A direct relation was observed between water sorption and Al₂O₃ contents of dolomites and limestones (Fig 19). The correlation coefficients are 0.899 for dolomites and 0.759 for limestones. This suggests that very good correlation exists between water sorption and alumina. It is seen that water sorption is a direct function of the amount of clay present in both the carbonate rock types. Error analysis has been done on the slopes of dolomites and limestones, which indicated that the slopes overlap and are statistically same but their intercepts are different.

According to the equation for the line of best fit, in dolomites water sorption increases from 0.03% to 0.21% for an increase in alumina content from 0.22% to 2.7%. On the other hand, water sorption increases from 0.02% to 0.76% for the above range of alumina content. This shows that limestones adsorb more water than dolomites at higher alumina content. Rogers (1976) has found similar relationship. His calculations have shown that limestones adsorb more water for equal amounts of alumina as compared to dolomites.

The fact that the limestones adsorb more water than dolomites probably depend on the different dispersion patterns of clay minerals in the interstitial spaces of dolomite crystals of the carbonate rocks. Dunn and Hudec (1966, 1972) proposed the concept of "rejection texture" in which they postulated that dolomite crystals during their growth in limestones tend to reject the clays to the grain boundaries, making the clays more or less continuous and hence, placing them in wettable position. They state that such rocks are highly adsorptive. Based on the rejection texture concept Rogers has concluded that concentration of clay at dolomite crystal boundaries may result in clustering of clay minerals with resultant decrease in the net effective surface area. In limestones where the clays are more dispersed, there would not be "interference" between clay minerals, resulting in a greater net surface area than in the dolomite.

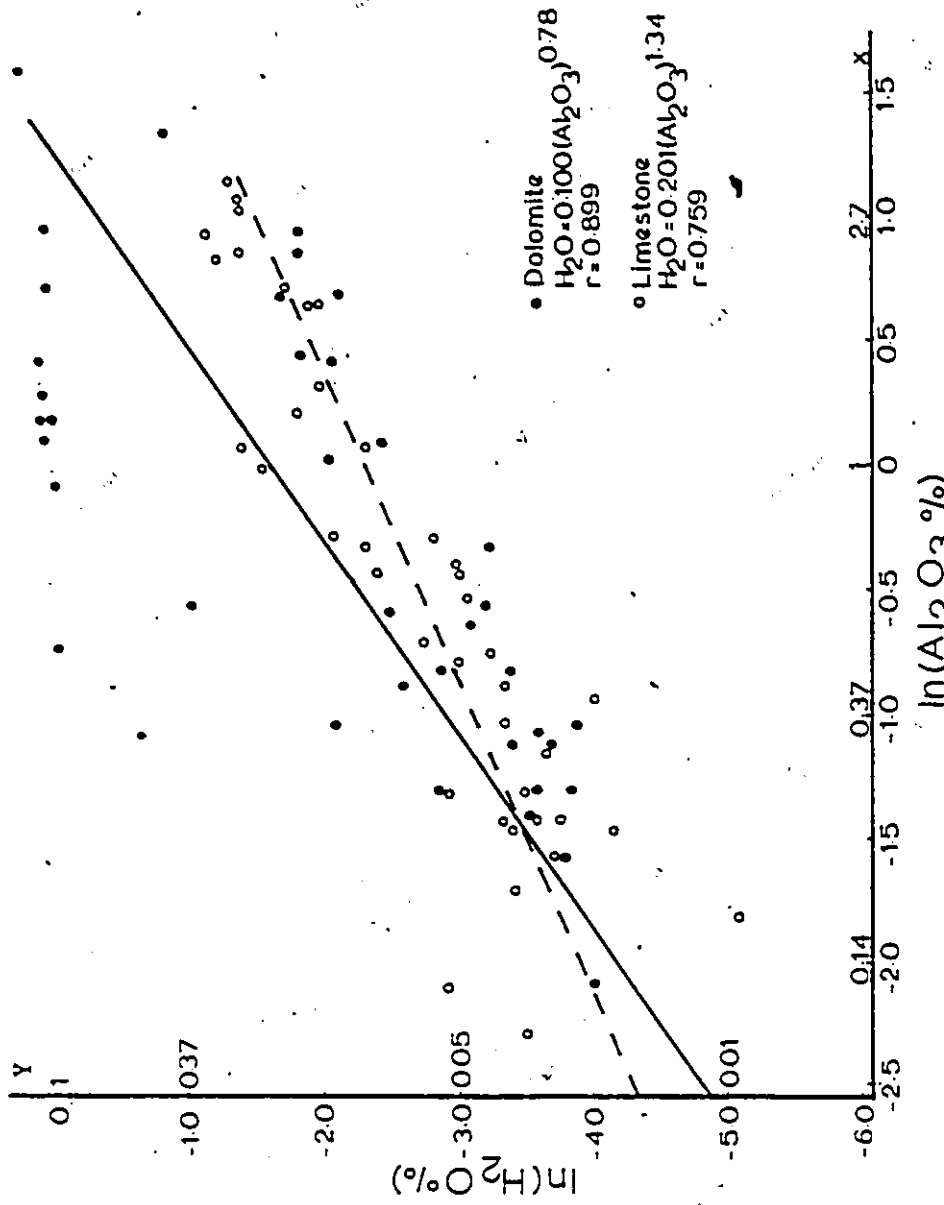


Fig 19 A plot of adsorped water (%) at 45% R.H vs alumina content for carbonate rocks

Another possible explanation is that the exchangeable cation on the clay surfaces in limestones is Ca and Mg on the clay surfaces of dolomite (Hudec personal communication). Ionic radius of Mg (.66 Å) is smaller than Ca (.99 Å). Ions with smaller radii possess higher surface charge compared to ions with large radii and therefore, bind to the clay surface firmly. It is obvious that other cations can more easily displace Ca than Mg. Therefore, it is quite probable that the water may tend to displace Ca ion with greater ease than Mg ion on the clay surface.

Copper Sorption

Cu vs CaO

No correlation between copper adsorption and CaO content was observed for dolomites or for limestones (Fig 20). Calculated correlation coefficient for dolomites and limestones is 0.08 and 0.237 respectively, which is much lower than the tabulated correlation coefficient of 0.325 at 5% significance level. Reasons for this lack of correlation are discussed below.

The explanation for the results observed in figure 20 is found in the reactivity of the carbonates with the metals. Heydemann (1959) reported that copper was adsorbed by clay minerals and quartz according to Freundlich adsorption isotherm whereas in the case of calcite a chemical reaction takes place. According to him calcite powder takes up copper ions from very dilute neutral aqueous solution through a chemical reaction and not through physical adsorption. Latter, Ashry (1973) found that there is correlation between copper and zinc adsorption and the clay-sized carbonate particles (calcite) of Nile River sediments. The above correlations according to him reveal that copper and zinc were bound to the clay-sized carbonate particles, and

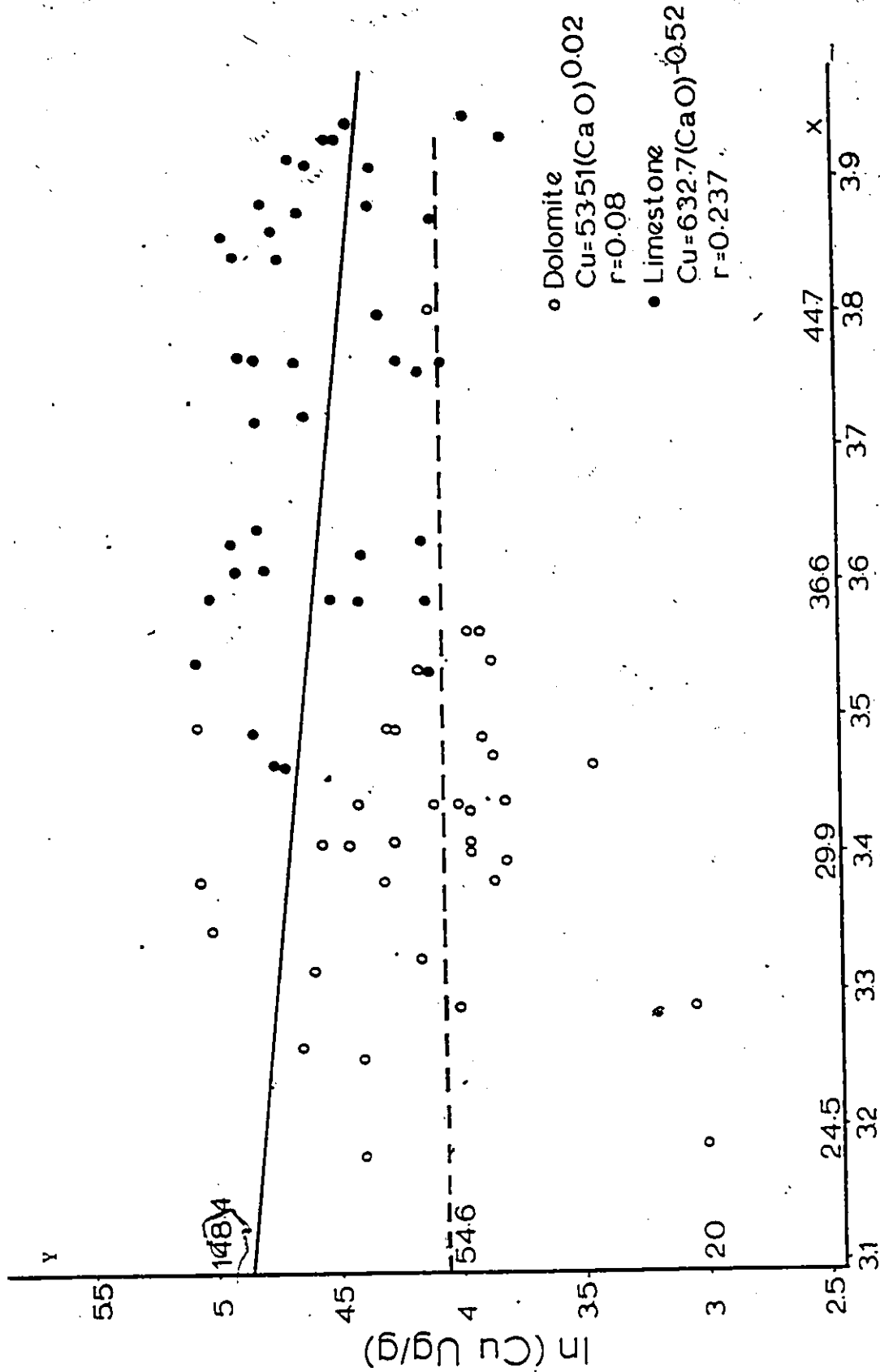


Fig 20 A plot of adsorbed Cu (ug/g) vs CaO content for carbonate rocks

the bonding between the carbonate particles and copper and zinc took place by means of chemical reaction. Therefore, it is quite obvious that calcite reacts with copper forming a compound of high solubility. Adsorption is not favoured if the adsorbate forms a compound of high solubility with the adsorbent (Mason 1966).

The flat lines in figure 20 are probably due to chemisorption. Similar type of flat lines were obtained by Smith and Fuzek (1946) and latter by Cook and Hackerman (1951) in the systems where chemisorption was operative.

Cu vs MgO

Limestones show a direct correlation between copper and MgO (Fig 21) whereas dolomites show an inverse relationship between copper sorption and MgO content (Fig 22). Similar relationship was observed between the water sorption and MgO content of the limestones (Fig 18). Earlier a direct relationship was observed between MgO and Al_2O_3 content of limestones (Fig 11). This suggests that there is a direct relationship between MgO and Al_2O_3 contents of limestones and Cu sorption.

In dolomites, the inverse relationship between copper and MgO contents is probably due to the fact that as MgO content increases the clay content decreases. The dependence of copper on clay content is shown in the following section.

Cu vs Al_2O_3

A direct correlation occurs between the copper sorption and Al_2O_3 contents of limestones and dolomites (Fig 23). Error analysis has been done on the slopes of dolomites and limestones, which indicated that the slopes are statistically same but their intercepts are statistically different and the relationships are also statistically different.

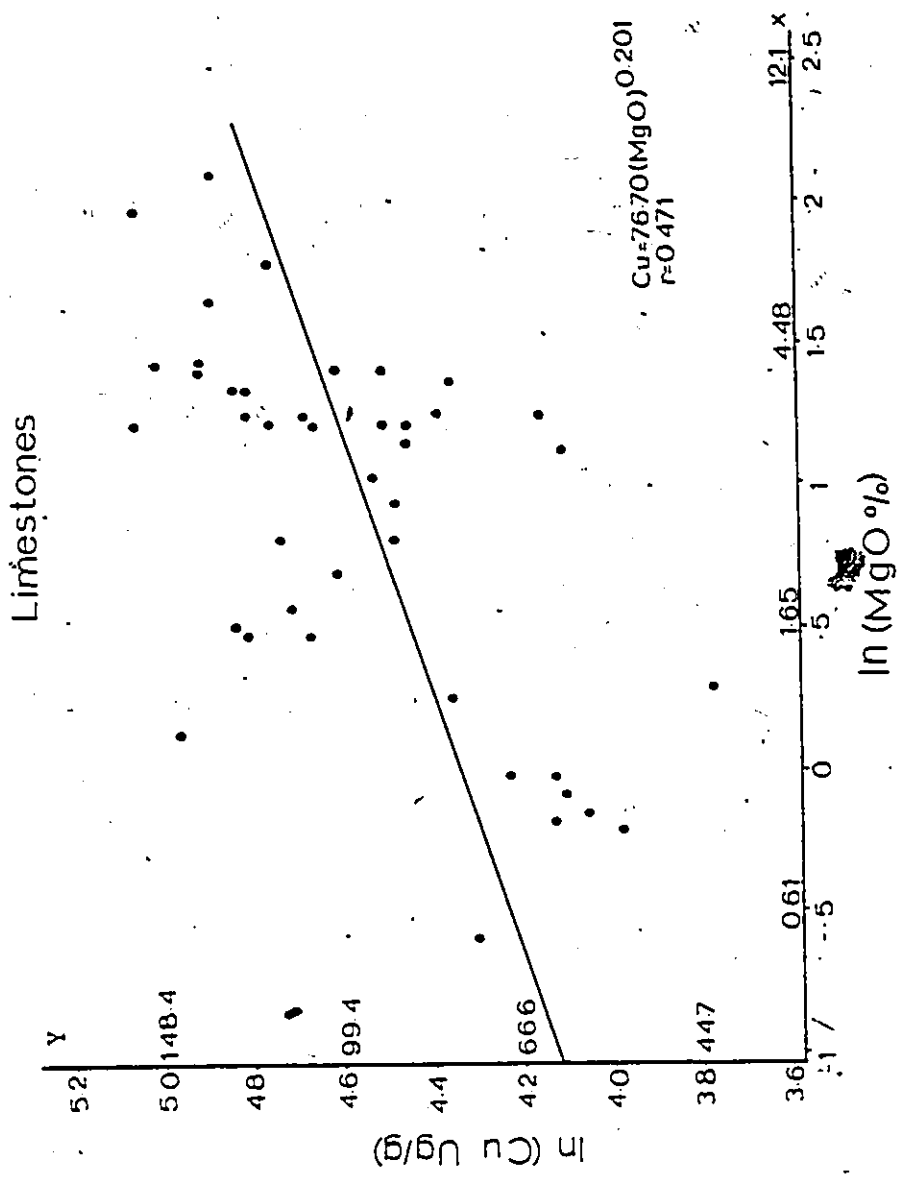


Fig 21 A plot of adsorbed Cu (ug/g) vs MgO content for Limestones .

Dolomites

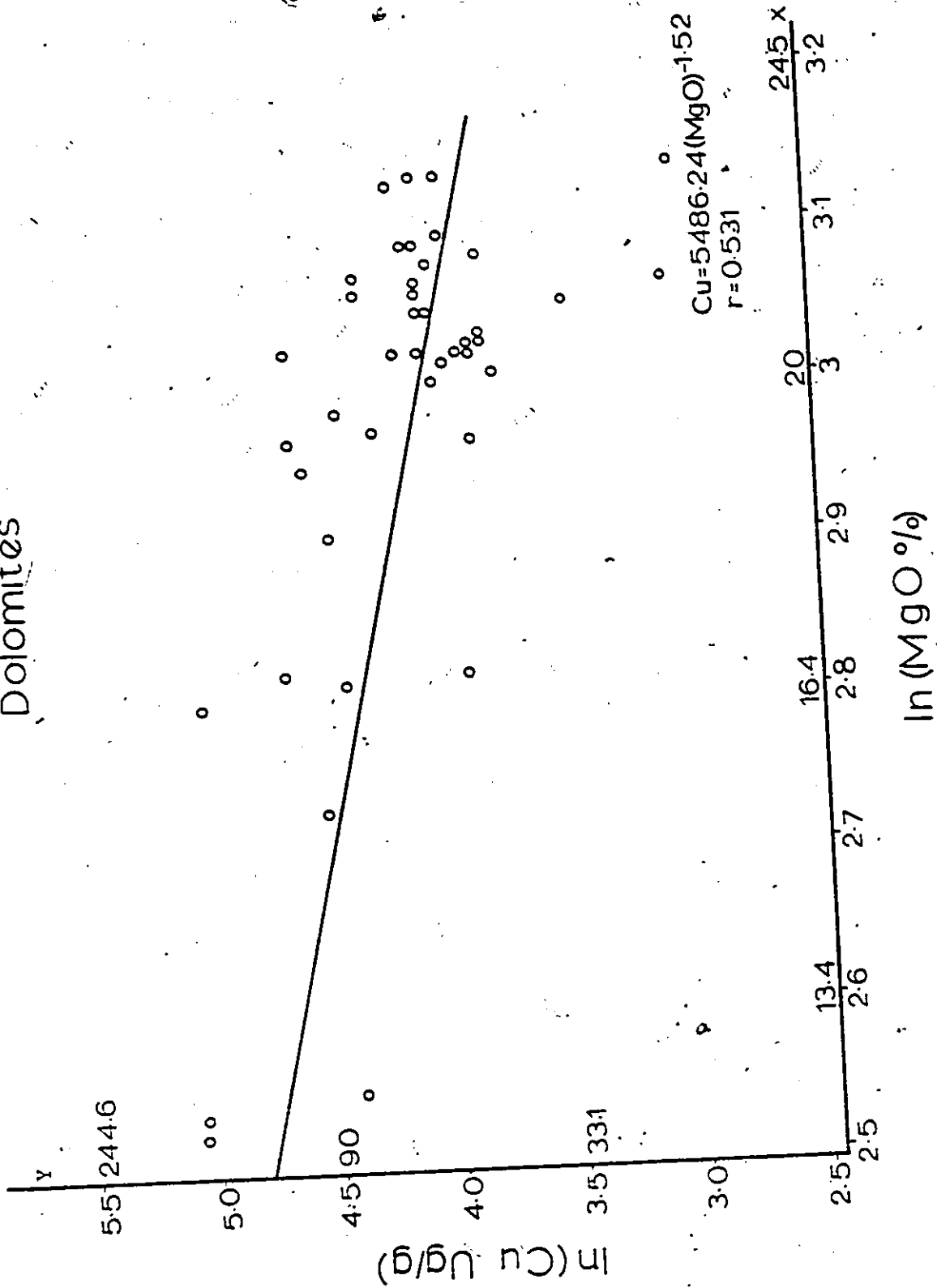


Fig 22 A plot of adsorbed Cu (ug/g) vs MgO content for dolomites

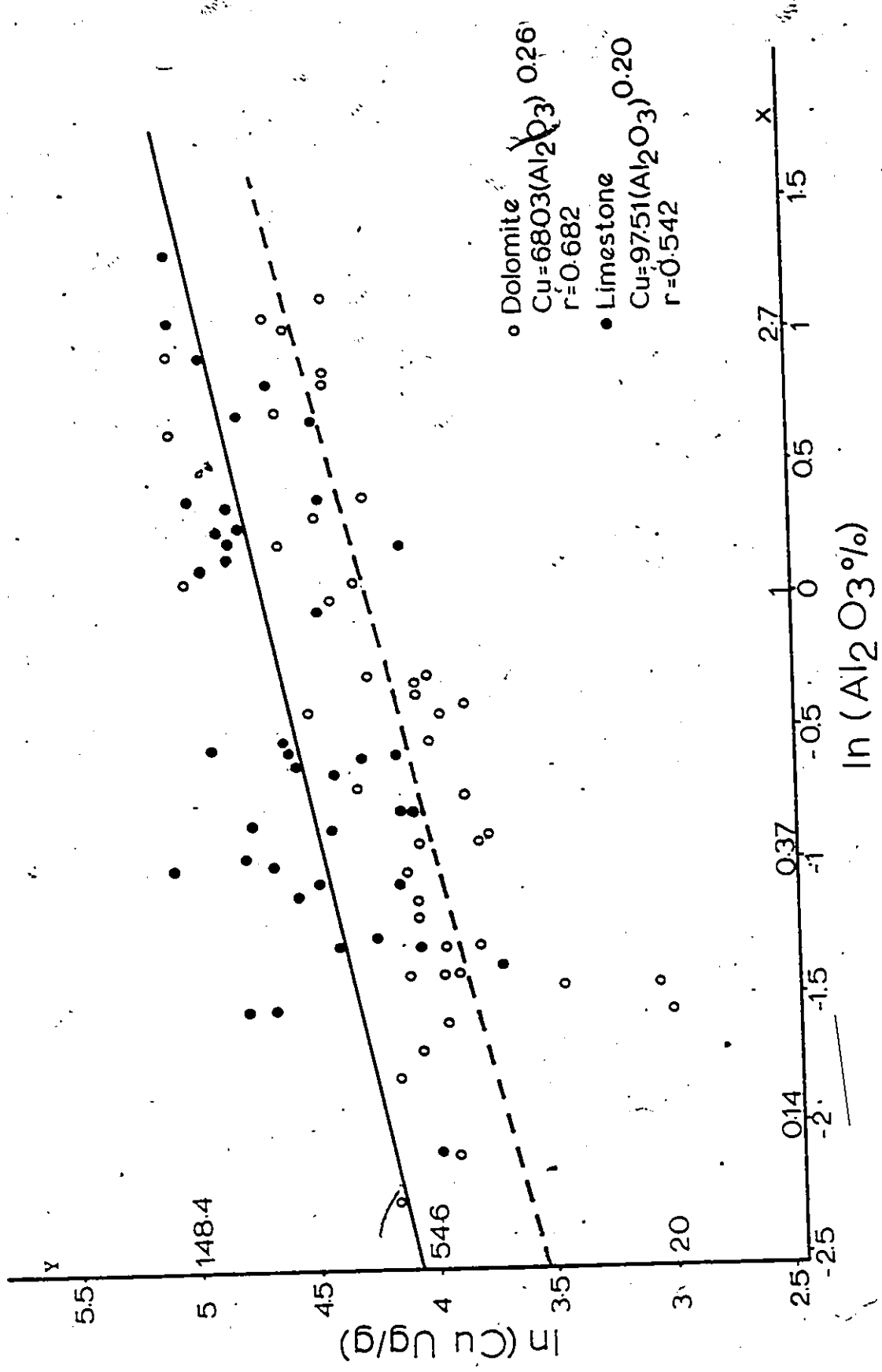


Fig 23 A plot of adsorbed Cu (ug/g) vs Al₂O₃ content for carbonate rocks

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According to the equation for the line of best-fit, in dolomites Cu sorption increases from 45.8 ug/g to 88.07 ug/g for an increase in Al_2O_3 content from 0.22% to 2.7%. In limestones Cu sorption increases from 72.03 ug/g to 118.93 ug/g for the above range of alumina content. The reasons for this are discussed below.

It is apparent that the copper sorption is a direct function of clay content of both the carbonate rock types. Although the overall clay content of the carbonate rocks does not exceed 1 to 2%, clay minerals play an important role in adsorption of metals and water. Calcite, dolomite and quartz assume a subordinate role owing to their relatively low surface area. Dunn and Hudec (1965) presented evidence that the major non-carbonate accessories such as clay and silica play a large part in sorption of water in rocks. Heydemann (1959) states that a suspension containing 0.01 weight percent of illite (a value frequently observed in the river water) extracts at pH 6.8 about 8% of the copper content from a solution with 0.3 ppm copper. The copper content decreases to 60 micrograms per litre. This illustrates the function and importance of clays in adsorption.

Clay minerals present in the carbonate rocks adsorb copper cations from a solution very efficiently. This is due to the unique physical properties of clay minerals such as high surface area, surface charge and high cation exchange capacity. Wayman (1967) states that maximum adsorption should occur at higher charge and small ionic size. The smaller the radius of a positive ion the higher its charge (Mason 1966). Copper with smaller ionic radius ($.72 \text{ \AA} \text{ Cu}^{2+}$) could be exchanged with ease for the exchangeable cations such as Ca, Mg and Na available on the clay surface whose ionic radii are comparatively larger than copper (Ca $.99 \text{ \AA}$ and Na $.97 \text{ \AA}$ Mason 1966).

Heydemann (1959) investigated adsorption of copper on clay minerals and has shown that adsorption increases in the sequence of kaolinite-illite-montmorillonite. The surface area of the respective clays also increases in this sequence, thus metal sorption is tied to surface rather than to the clay mineral type.

As shown in figure 23 limestones adsorb slightly more copper than dolomites. Similar relationship was observed with water. This may be attributed to the "rejection texture" phenomenon. This aspect was discussed earlier with respect to the direct relation between water and Al_2O_3 as shown by limestones and dolomites (Fig 19).

Another possible reason for the disparity in the adsorption characters of the two carbonate rocks could be as follows: The exchangeable cation is Ca on the clay surface in limestones and Mg on the clay surfaces of dolomites (Hudec personal communication). If copper ion is introduced its ability to dislodge existing cations (such as Ca and Mg) on the clay surface will be proportional to the size ratio between the two. Mg ion is smaller (.66 Å) than Ca ion (.99 Å) hence, exerts higher surface charge. Therefore, Mg ion binds to the clay surface firmly. Copper can displace Ca ion with greater ease than it will displace Mg.

Lead and Zinc Sorption

Lead and zinc have similar geochemical behaviour and are discussed together.

Pb and Zn vs CaO

There is a weak correlation between Pb and the CaO content of limestones (Fig 24). However, despite of the weak correlation, it is considered that there is no relationship between the Pb sorption and CaO content of limestones.

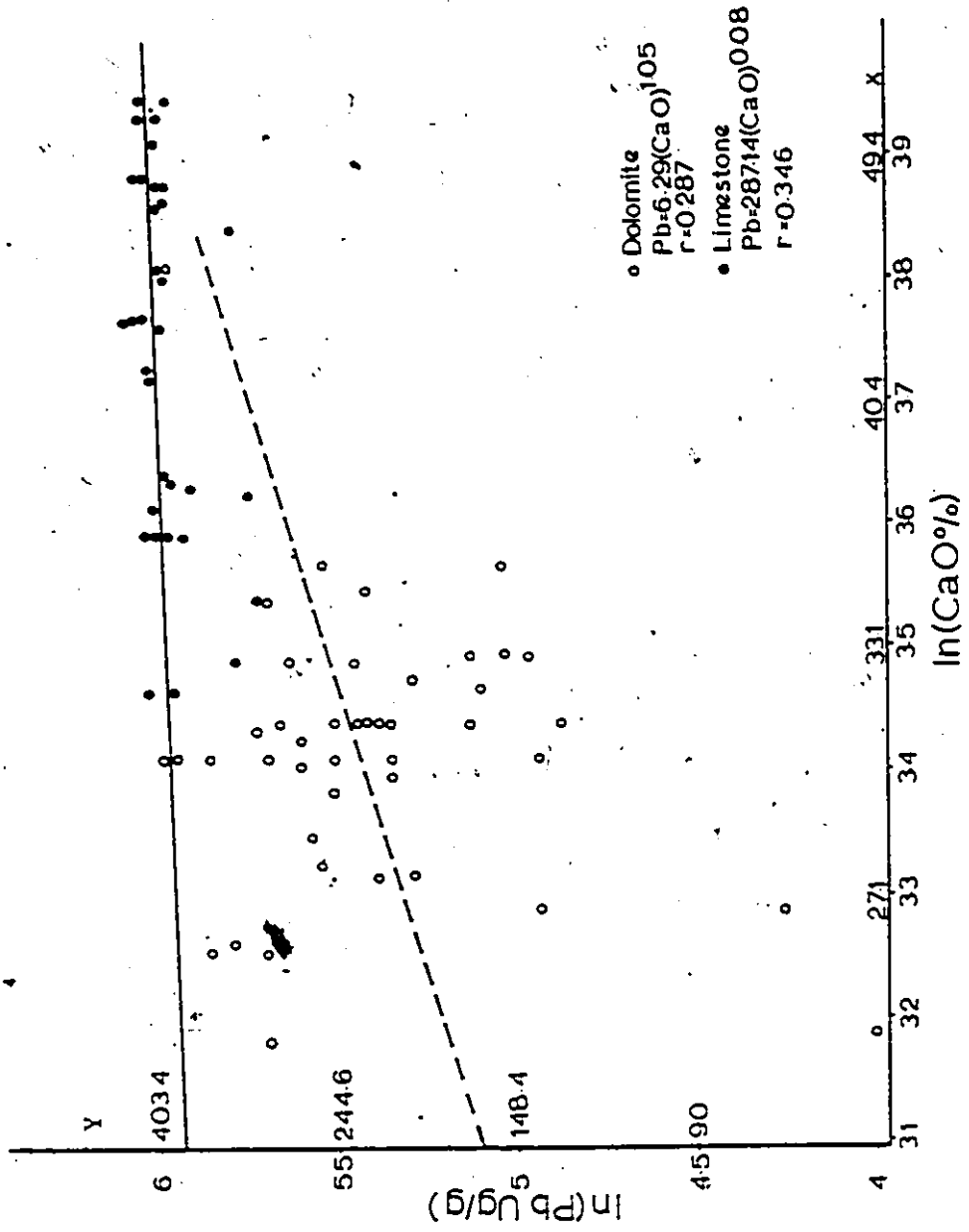


Fig 24 A plot of adsorbed Pb ($\mu\text{g/g}$) vs. CaO content for carbonate rocks

Likewise no correlation was observed between the Zn sorption and CaO content of limestones (Fig 25).

The lack of correlation in the above two cases may be attributed to chemisorption. Kipling (1965) has found chemisorption to occur in a number of systems during adsorption at room temperatures. Smith and Fuzek (1946) during their studies on adsorption of palmitic acid have shown in their plot a typical curve where chemisorption was operative, obtained a flat line similar to the flat lines derived in the above two figures. Cook and Hackerman (1951) have obtained two sets of curves while studying the acid sorption, a flat line for stearic acid where chemisorption was operative, and another with a positive slope where physical adsorption was operative. The flat lines in the above two figures without any correlation mean that chemisorption was operative.

Jurinak and Bauer (1956) have investigated the thermodynamics of zinc adsorption on calcite, dolomite and Ca-magnesite and found that about 10% of the adsorption sites probably available on calcite were occupied by zinc when the equilibrium Zn^{++} aqueous concentration was $0.90 \times 10^{-6} M$ at $25.1^{\circ}C$. The Ca-magnesite shows a somewhat greater affinity for Zn ion than calcite, while dolomite is intermediate.

Ashry (1973) reported a direct correlation between metal (Cu and Zn) sorption and clay sized grains of calcite. The finely dispersed carbonate particles acted as accumulators for copper and zinc. He stated that the bonding between the carbonate particles and copper and zinc took place by means of a chemical reaction. This indicates that zinc could be chemically sorbed by carbonates. Same analogy could be applied for lead also.

It has been observed earlier that an inverse relationship occurs between water sorption and CaO content in both the carbonate rock types (Fig 16).

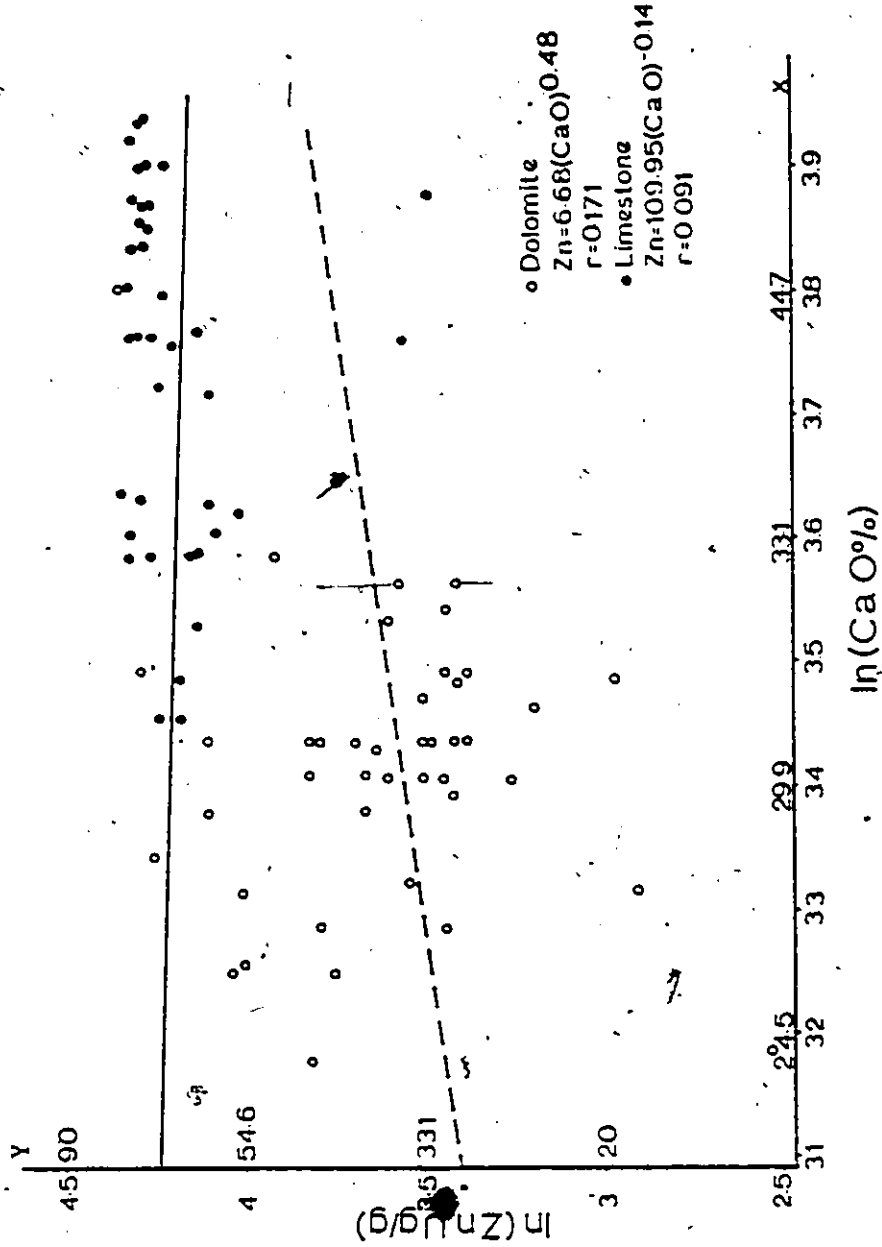


Fig 25 A plot of adsorbed Zn (ug/g) vs CaO content for carbonate rocks

Therefore, in this case water sorption is independent of lead and zinc sorption since these two elements are chemically adsorbed by the calcite content.

Pb and Zn vs MgO

No correlation between lead and zinc sorption and MgO content of limestones was observed (Figs 26 and 27). Lack of correlation can also be attributed to the chemisorption.

A direct relationship exists between water sorption and MgO contents of limestones (Fig 18). Water sorption therefore, is independent of lead and zinc sorption with regard to MgO content of limestones.

An inverse relationship between lead and zinc sorption and MgO content of dolomites was seen (Figs 28 and 29).

This suggests that the dolomites are more surface active and less chemically reactive than the limestones. Jurinak and Bauer (1956) observed that in adsorption of zinc on mineral dolomite, the surface reaction differs noticeably from the reaction occurring in the calcite system. No surface saturation was evident in the concentration range of zinc used and an increase in temperature caused an increase in the adsorption of zinc. This indicated a difference in the relation of zinc ion to the dolomite surface. Zn content of Calcite decreases with increasing temperature, indicating an exothermic reaction, i.e. a chemical reaction with the liberation of heat. This suggests that the calcite takes Zn by chemisorption.

Another probable reason for the decreased sorption of lead and zinc with the increased MgO could be explained by the fact that the Al_2O_3 content decreases with increase in MgO content (Fig 10), therefore, lead and zinc sorption also decreases.

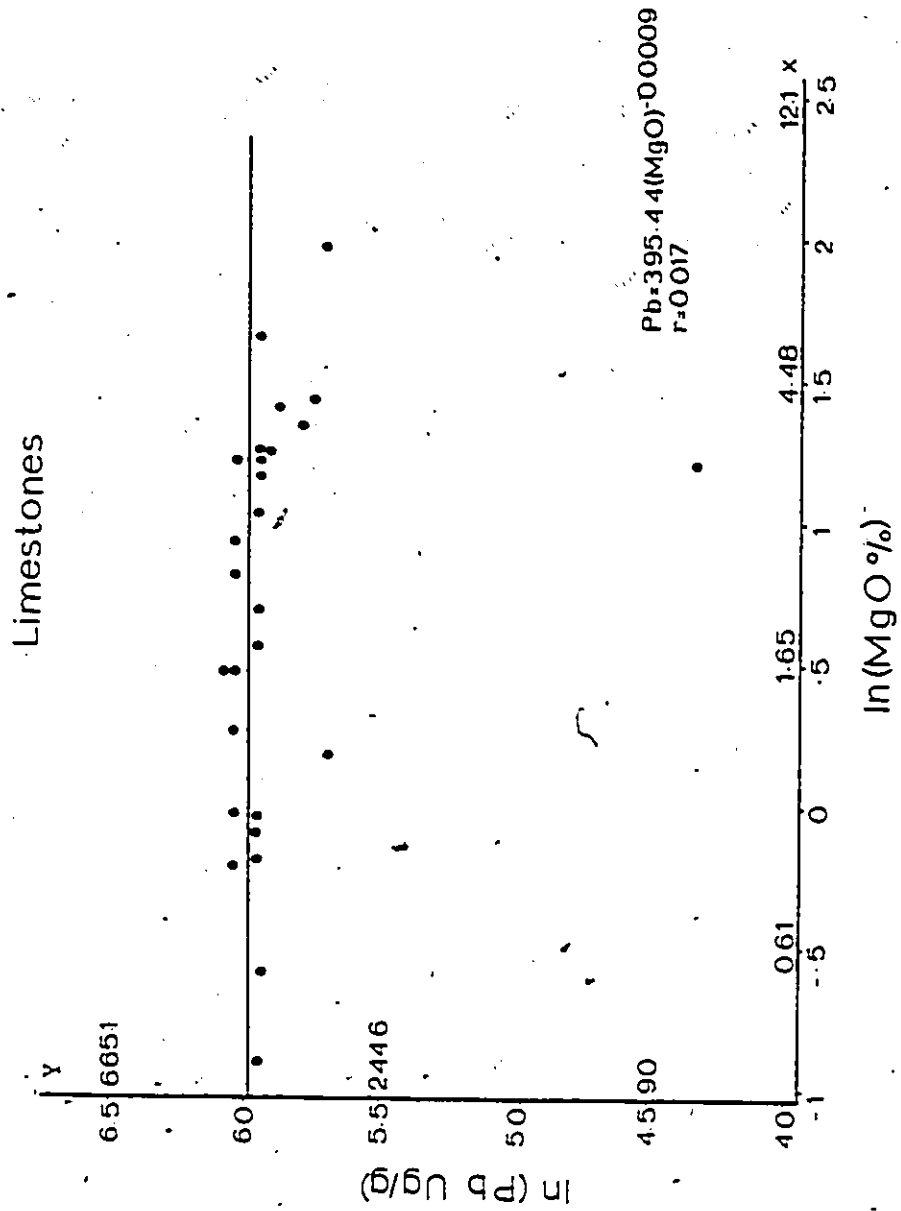


Fig 26 | A plot of adsorbed Pb (ug/g) vs MgO content for limestones

Limestones

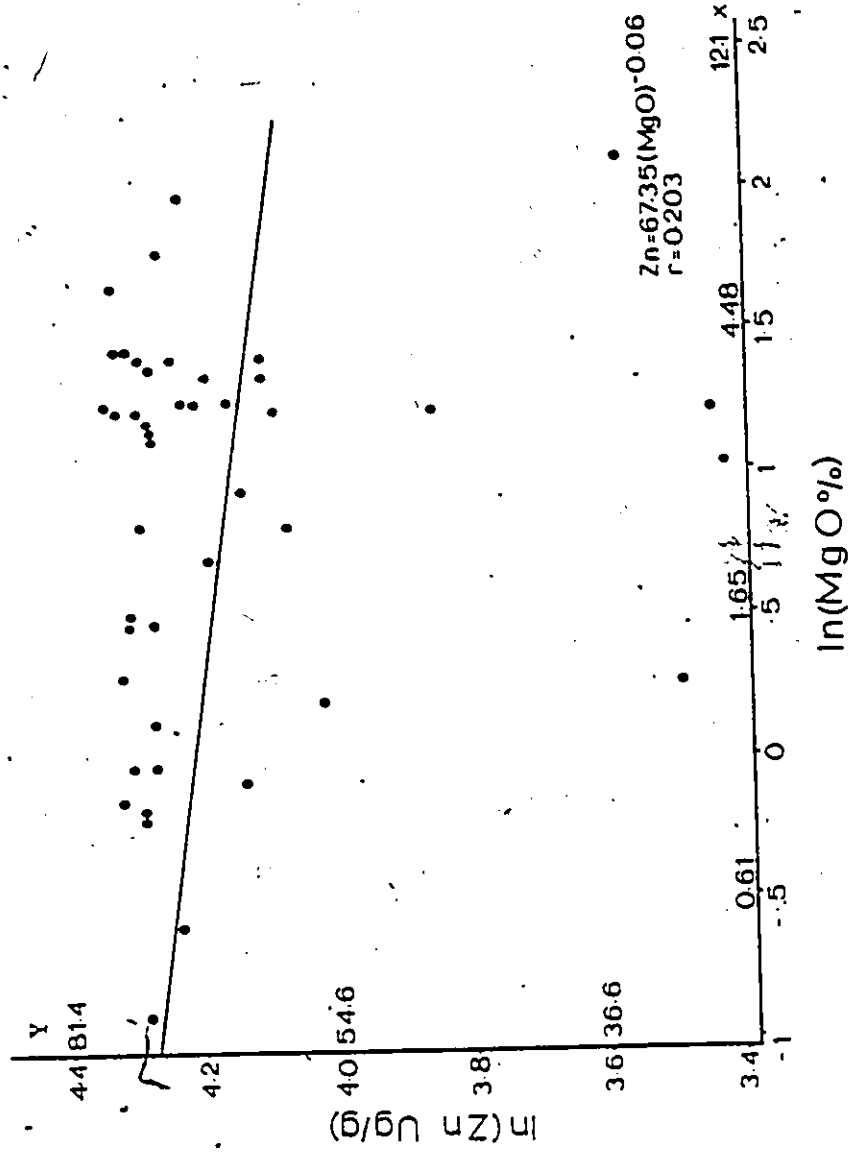


Fig 27 A plot of adsorbed Zn (ug/g) vs MgO content for Limestones

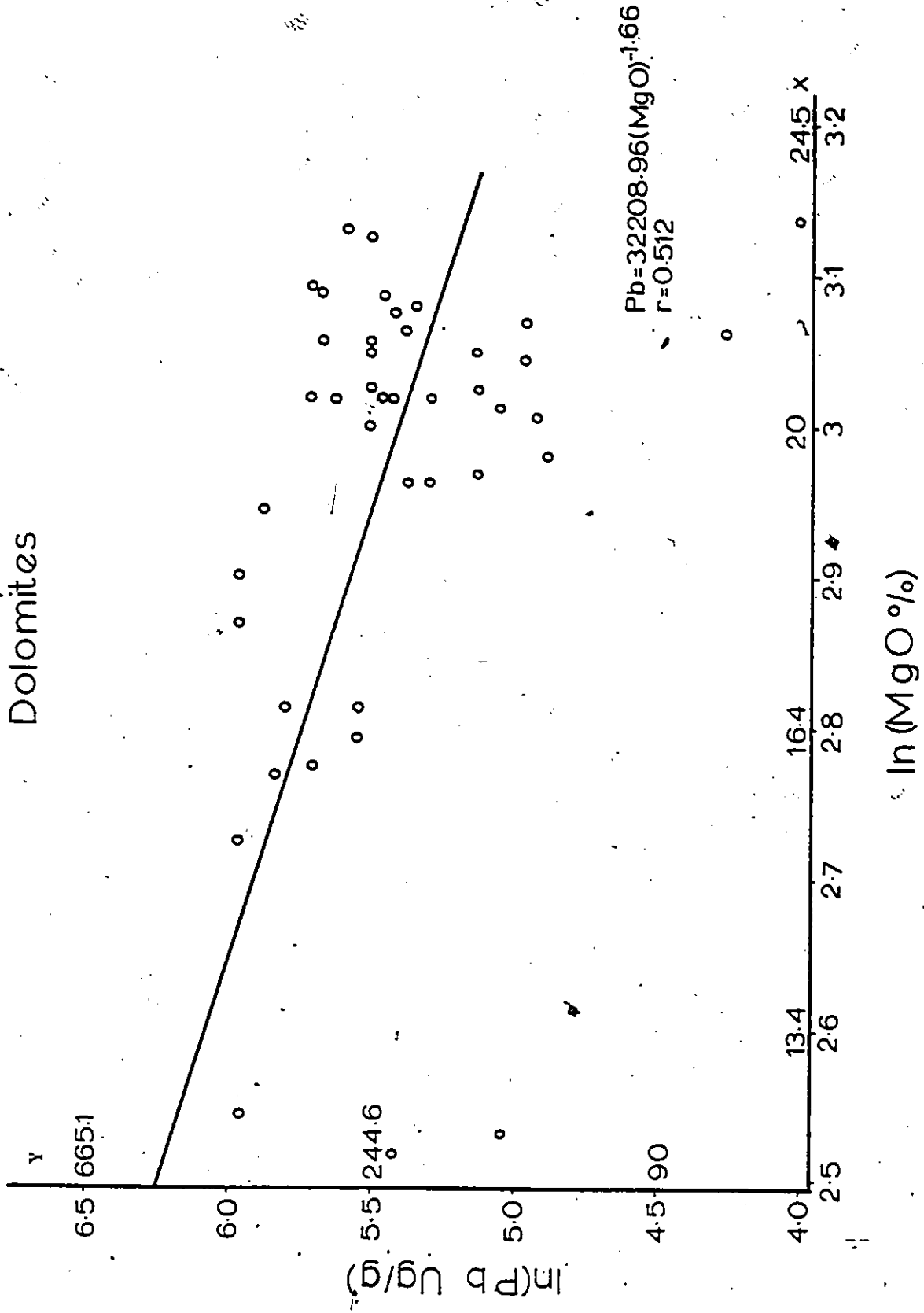


Fig 28 A plot of adsorbed Pb (ug/g) vs MgO content for dolomites

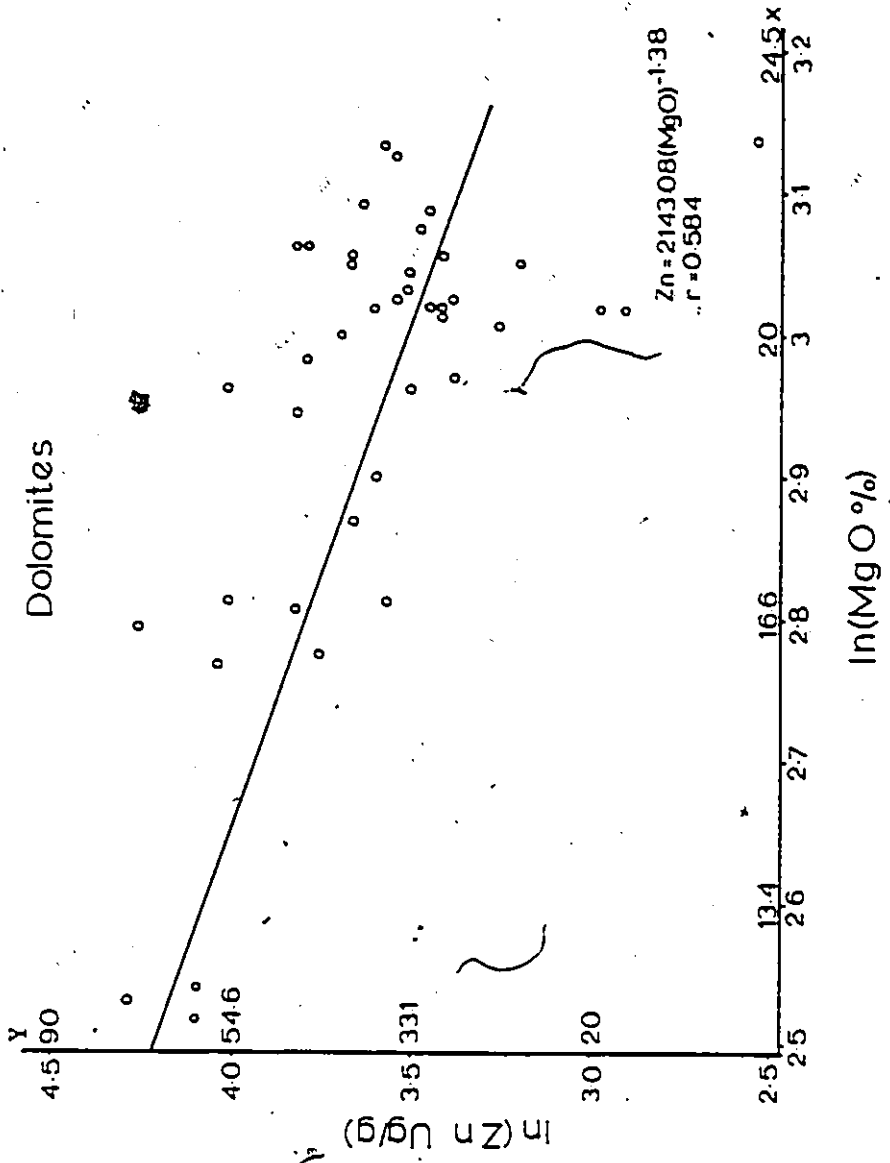


Fig 29 A plot of adsorbed Zn (ug/g) vs MgO content for dolomites

Pb and Zn vs Al₂O₃

For limestones there is no correlation between lead, zinc and Al₂O₃ content (Fig 30 and 31). This lack of correlation can be interpreted as a function of chemisorption rather than adsorption.

The flat lines in the above two figures would indicate that chemisorption was operative. If chemisorption is operative in a system no matter how much clay is present in the rock a relation could not be obtained between clay and metal sorption. Calcite, a dominant mineral in the limestones, would react easily with lead and zinc, resulting in the formation of carbonates of lead and zinc, and thereby obscuring the physical adsorption of metals by clays.

A direct significant relationship between lead and zinc sorption and Al₂O₃ content of dolomites was observed (Figs 30 and 31). Error analysis has been done on the slopes and intercepts of dolomites and limestones, which indicated that the slopes and intercepts are statistically different; and the relationships are also statistically different. According to the equation for the line of best fit, lead sorption increases from 196.87 ug/g to 254.67 ug/g and the zinc sorption increases from 30.65 ug/g to 38.47 ug/g for an increase in alumina content from 0.22% to 1%. This means that more lead was sorbed by alumina than zinc. This is not in agreement with the work of Krauskopf (1956) who has experimentally demonstrated that clays adsorb 99% and >96% zinc and lead respectively. He maintained a pH of 7.7-8.2 and a temperature range 18° to 23°C and concentration of adsorbent (clay) was maintained same (20 g/litre). However, the initial concentrations were 2.0 ppm and 0.5 ppm for zinc and lead respectively. The discrepancy between relative amounts adsorbed in this work compared to Krauskopf's is probably a function of the relative difference in concentration of lead and zinc used. The amount of a substance adsorbed

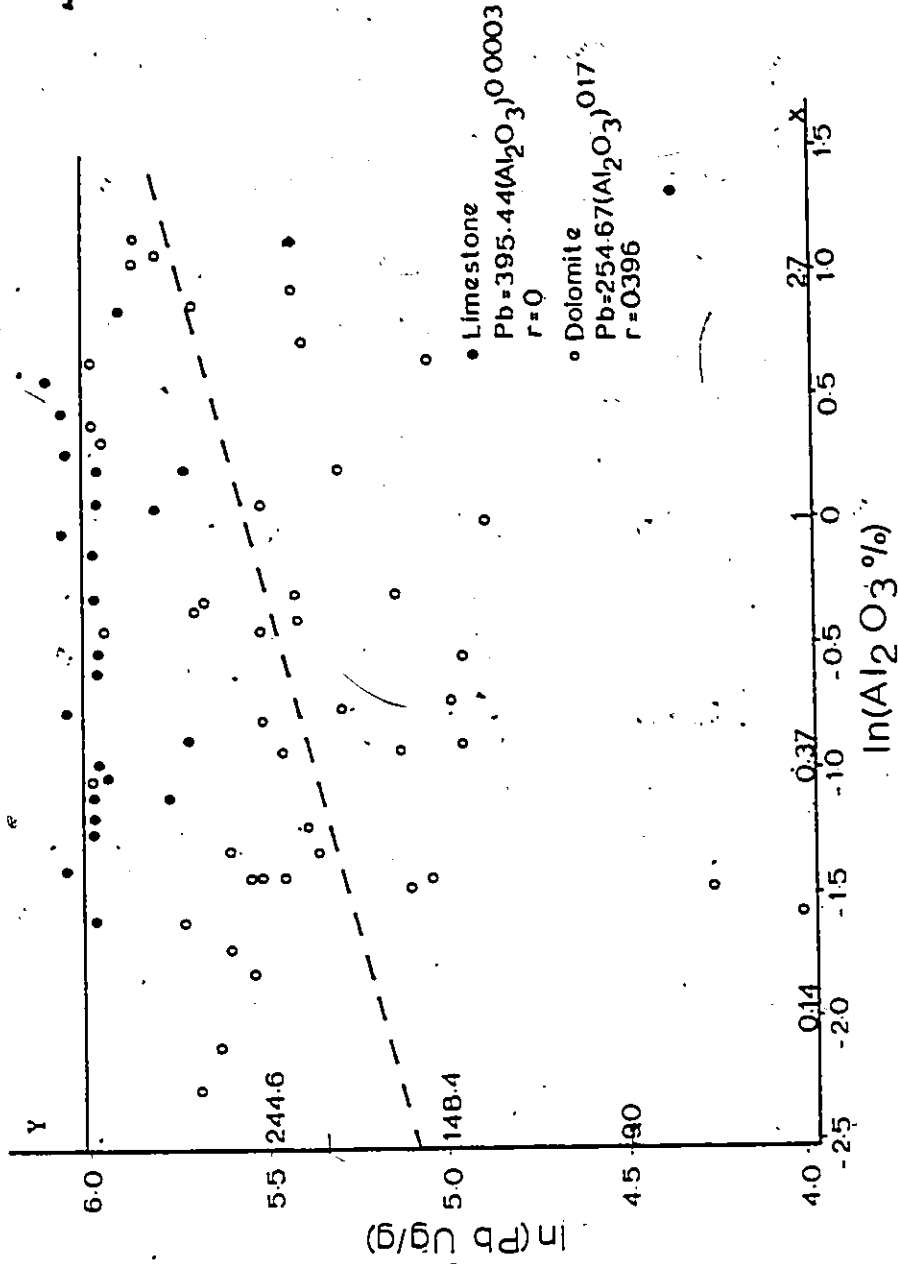


Fig 30 A plot of adsorbed Pb (ug/g) vs Al₂O₃ content for carbonate rocks

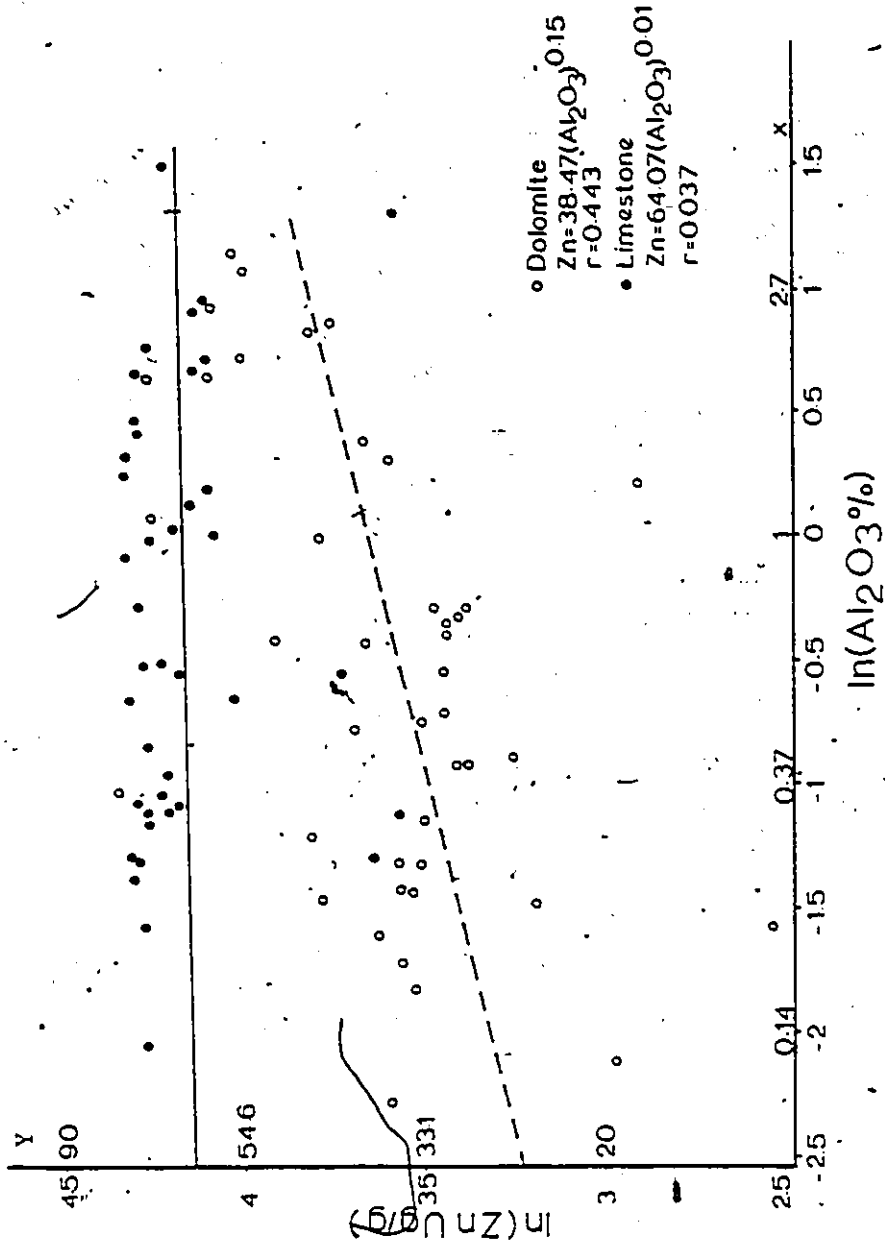


Fig 31 A plot of adsorbed Zn (ug/g) vs Al₂O₃ content for carbonate rocks

from a solution increases with its concentration in solution (Mason 1966).

More lead could have been adsorbed if lead concentration was maintained the same as that of zinc concentration.

Explanation is needed as to why more lead was adsorbed than zinc. Atomic weight may be the controlling factor in the adsorption. Atomic weight of Pb is 207.19 and that of Zn is 65.37. Zn is divalent whereas Pb functions as divalent and trivalent element. Choudhury and Bose (1971) reported that metal adsorption (w/w) by the humic fraction of soil was governed by the atomic weight and valence of the elements. The relative adsorptions of the elements with the same valence were proportional to their atomic weights. Thus, about the same amount of Cu, Zn, Co and Ni was adsorbed, whereas 3.5 times (w/w) as much Pb was adsorbed. They concluded that atomic weight of Pb is 3.1 times greater than Zn, and therefore, 3.5 times (w/w) lead was adsorbed. This explains as to why more lead than zinc has been adsorbed in the experiments reported here.

The direct significant relationship between Cu, Pb, Zn and Al_2O_3 in dolomites (Figs 23, 30 and 31) is in agreement with the water sorption (Fig 19); therefore, copper, lead, zinc and water sorption are interrelated with each other and depend on the Al_2O_3 (clay) content in dolomites. In dolomites a much better correlation exists between water and alumina ($r = 0.899$) than metals and alumina ($r = 0.682, 0.442$ and 0.396 for copper, zinc and lead respectively). On the other hand in limestones, a good correlation occurs between water and alumina ($r = 0.759$) and copper and alumina ($r = 0.542$). No correlation occurs between lead, zinc and alumina content of limestones. Water has better correlation with alumina content than metals because water is adsorbed not only to the clay surface but also to the exchangeable cations.

CHAPTER 7

DISCUSSION OF RESULTS IN RELATION TO FIELD CONDITIONS

The occurrence of lead and zinc deposits in carbonate rocks is well known. These are the so called "Mississippi Valley" type of deposits of North America or "Alpine" type of Europe. The process, mode and other conditions of mineralization are the same the difference is only one of nomenclature. The most frequent host rocks for these deposits are mainly dolomites, but may also be magnesian limestones and pure limestones. A review of the pertinent literature reveals a number of possible alternatives for the genesis of lead and zinc deposits in carbonate rocks. The following is a summary of some of the ideas expressed by different workers.

At Pine Point in northwestern Canada much of the sphalerite and galena were deposited partly as fillings in cavities and partly as replacements of the dolomite (Campbell 1967).

Geldsetzer (1971) believes that syngenetic dolomitization of the brecciated carbonate rocks and sulphide mineralization is responsible for the lead-zinc mineralization in northern Baffin Island, N.W.T., Canada.

Callahan(1967) states that the Mississippi Valley type of deposits in U.S.A and Canada are spatially localized in the carbonate rocks. These deposits are further characterized by an association with dolomites in many instances.

During his studies of the lead-zinc occurrences in the northern limestone Alps, Schneider (1953) recognized that the strata in which the ores were bound consisted of a "special facies" that include, pure dolomite,

laminated dolomite-calcilutite, laminated bituminous dolomite-calcilutite and greenish marl.

Smirnov (1967) reported on the superimposed molds of the post-Caledonian platform in central Kazakhstan, U.S.S.R where stratiform deposits of lead and zinc are well known among upper Devonian strata of dolomitized limestone.

The above examples illustrate that there is an association between lead-zinc mineralization and dolomite rocks rather than other carbonate rocks. Equally well there is also an association between lead-zinc and copper mineralization and shales and similar rock types. A review of the following deposits suggests the Pb-Zn-Cu shale association.

The lead-zinc deposits of MacArthur River, Australia, occurs in black carbonaceous-dolomitic-pyritic shales (Cotton 1965).

At Mt. Isa, Australia, the lead-zinc deposits occur in the pyritic Urquhart Shale Member of the mount Isa Group (Stanton 1972).

According to Dunham (1964), copper with some lead and zinc occurs in the Kupferschiefer formation which is a bituminous-calcareous or dolomitic shale. The ore deposits possibly represent an adsorption of metallic elements from sea-water.

Mendelsohn (1961) reported that the copper in the Roan Province of Zambia, occurs mainly in the so called Ore Shale, which lithologically varies from a shale to a fine silt and from slightly to conspicuously carbon bearing. Most of the sulphide of the ore is found in this shale, some notable quantities of ore occur occasionally in the associated dolomites and arenites of this units.

The Redstone deposit in Mackenzie Mountains (Green and Godwin 1963 and 1964, Gabrielse, Roddick and Blusson 1964) is a bedded copper deposit. It occurs mainly in three persistent green carbonate rich beds within a sequence of Hydrinian mudstone and siltstone.

The present study shows that the relative metal sorption (by weight) by clays in the dolomites increases in the order of $Pb > Cu > Zn$. Lead is adsorbed more than copper and zinc. No correlation was found in limestones between the lead, zinc and Al_2O_3 contents. In dolomites copper sorption increases from 45.8 ug/g to 88.07 ug/g for an increase in alumina content from 0.22% to 2.7%. In limestones copper sorption increases from 72.03 ug/g to 118.93 ug/g for the above range of alumina content. In dolomites lead sorption increases from 196.87 ug/g to 254.67 ug/g and zinc sorption increases from 30.65 ug/g to 38.47 ug/g for an increase in alumina content from 0.22% to 1%.

Krauskopf's (1956) adsorption experiments have shown that the metal adsorbed by clays was 99% zinc, 96% lead and 94% copper. More zinc was adsorbed than lead and copper and this does not correspond with the present work. His concentrations of solutions were 2 ppm, 0.65 ppm and 0.5 ppm zinc, copper and lead respectively. The reason for the greater adsorption of zinc is probably due to its higher concentration in the solution. It is one of the rules of adsorption that the amount of a substance adsorbed from a solution increases with its concentration in that solution (Mason 1966). Although the concentration of copper (0.65 ppm) was higher than that of lead (0.5 ppm) more lead was adsorbed. This is probably due to the time difference that was allowed in his experiments by Krauskopf. He allowed 3 days in the case of lead and zinc and only 2 days in the case of copper. Perhaps if the copper experiment was allowed to proceed for one more day more copper could have been adsorbed from solution. In the experiments by

Garber the concentrations of solutions used were 500 ug/ml lead, 200 ug/ml copper and 100 ug/ml zinc, and therefore, more lead was adsorbed followed by copper and zinc.

Krauskopf states that, in general the amount of adsorption in a particular case depends not only on temperature, pH and salinity as (does solubility) but on the time of standing, amount and physical state of the adsorbent, and concentration of adsorbed ions as well. Steger (1974) has demonstrated similar results for the adsorption of copper and zinc on bentonite clay. He stated that the amounts adsorbed depend on the nature and concentration of the metal ions present, the pH of the medium, the amount of clay used and the contact time of the clay with the medium.

The concentrations of lead, zinc and copper used by Garber were selected on the basis of the concentration of these elements found in some natural water. The recent "ore forming solutions" of the Salton brine pool (Skinner et al. 1967) contained the following metals:

	Bore No. 1 II D	Bore No. 2 II D
Cu	8 ppm	3 ppm
Pb	84 ppm	80 ppm
Zn	790 ppm	500 ppm

The Red Sea brine pools (Degens and Ross 1969) contained the following metals:

	Atlantis	Discovery
Cu	2.6×10^{-4} ppm	7.5×10^{-5} ppm
Pb	5.4×10^{-6} ppm	7.7×10^{-4} ppm
Zn	6.3×10^{-4} ppm	1.7×10^{-5} ppm

White (1968) has compiled chemical analysis data reported by various workers and gave the following values for Atlantis and Discovery pools of the Red Sea Geothermal system.

	Atlantis II	Discovery
Cu	0.8 ppm	< 0.4 ppm
Pb	0.5 ppm	< 0.014 ppm
Zn	0.5 ppm	0.5 ppm

In the Mississippi Valley deposits, the information on the composition of the mineralizing solutions comes from fluid inclusions. Czamanske et al (1963) found by neutron activation that the inclusion fluids in fluorite contained 150 ppm copper and 570 ppm zinc.

Garber's metal concentrations for the present experiments were 200 ug/ml copper, 500 ug/ml lead and 100 ug/ml zinc. This is below the metal contents of the Red Sea brines, but is similar to the metal contents of Mississippi Valley and the Salton Sea brines. Moreover, Garber has done a search of the literature on the metal contents of the oil field brines and selected the metal content of his solutions as approximately of oil field brines. Thus there is a rationale for the selection of the lead, zinc and copper concentrations as made up by Garber.

Based on fluid inclusion studies White (1968) proposed a connate origin for the ore fluids of Mississippi Valley type ores. Hall and Friedman (1963) have provided evidence for a dominance by connate water during the main stages of deposition of fluorite sulphide minerals in Mississippi Valley deposits. Jackson and Beals (1967) suggested two types of connate water in forming the above deposits, base metals were transported in sulphide

deficient brines escaping from deep sedimentary basins. H₂S rich brines from shallow depths mixed with the metal bearing brines and precipitated metals.

The composition of the brines found in inclusions is actually similar to the oil field brines of the Mississippi Valley (Meents et al. 1952, White et al. 1963). The Na-Ca-Cl brines are probably marine connate waters (White 1968). Similarly, Heyl et al. (1974), on the basis of isotope data concluded that the main ore fluids were heated oil-field brines. They believed that ore fluids are of connate or evaporite sulphate origin.

According to White (1968) the Salton Sea Geothermal system brine is ground water that dissolved salts and metals from the associated evaporites and clastic sediments

Whatever the source of the ore solutions may be the above examples show that the metals are associated with saline solutions and this is true with respect to past and present mineralizing solutions. Fluid inclusions of the Mississippi Valley contained on the average 15 to 20% dissolved salts (Roedder 1963, Hall and Friedman 1963). The salinities of Red Sea and Salton Sea brines are very similar and contain 25% of dissolved salts. Garber has prepared his solutions in distilled water. Whereas in the natural systems metals occurred in salt solutions. Hudec et al (1976) have shown that adsorption of copper increases with the increase in salinity. Lead and zinc exhibit a reverse behaviour to that of copper. They believe that the deposition of the metal from the salt solution is not governed by the internal surface area of the samples, but some other considerations such as salt concentration in the solution, chemistry of the rock, pH-Eh.

relationships imposed by the dissolved salts etc. Therefore, adsorption of metals in natural systems may be different from the adsorption experiments that were carried out with distilled water in the present study. Presence of salt would affect the solubility, pH and other conditions.

The pH conditions that prevailed during the Mississippi Valley ore deposition can also be obtained from the fluid inclusions. However, reliability of the data obtained is questionable. Roedder (1967 b) commented that many quantitative measurements of inclusion pH that have been reported in the literature are probably invalid (most of them). They were usually made on the water solution obtained by leaching the crushed mineral and such solutions do not contain gases under high pressure as originally present. The inclusion fluid has been in contact with the host mineral and possible impurity minerals that may affect the pH. Roedder believes that a few measurements that were made on inclusion fluid, in part with simple litmus, are probably more significant. Erickson (1965) has thus determined the pH of large inclusions in calcite from the upper Mississippi Valley lead-zinc deposit to be 7.5. Anderson (personal communication 1978) from thermodynamic calculations established a lower pH of 4. The upper pH limit is <6.

The overall pH values for the Salton Sea brine is close to 5.5 as measured at 25°C and 4.6 as calculated for 300°C by Helgeson (1967). The pH conditions of the Red Sea brines vary from 5.3 (?) to 6.2 at 20°C for the Atlantis II and Discovery pools, respectively (White 1968). Garber has maintained a pH of 5 at room temperature in order to prevent precipitation of metals. This value is therefore in line with the pH range of values for the Salton Sea and Red Sea, and the Mississippi Valley depositional fluids.

The pH value has a definite function in the adsorption of metals. Heydemann (1959) found that adsorption capacity of clays increases with increasing pH as well as concentration. His figures show that more copper was adsorbed at 6.8 than at 5.1 pH (Figs 2-A, 3-A and 4-A). Steger (1974) has shown from his experiments on copper and zinc adsorption by bentonite clay that adsorption increases with increasing pH. His figures showed that more of copper and zinc was adsorbed at pH 5 than 4. The decrease in the adsorption of copper and zinc with increasing acidity is due to the decrease in the dissociation of the sorption sites (Steger 1973). Therefore, the adsorption process in natural solutions would be more effective under higher pH conditions (5.5., 6.2 and 7.5) than in the laboratory conditions performed by Garber with a pH of 5.

The temperature of formation of the Mississippi Valley type of deposits as shown by fluid inclusion geothermometry shows that temperatures in most deposits were relatively low ranging from 70° to 135°C for inclusions in sphalerite of southern Illinois and Kentucky (Pinckney 1966, Roedder 1972). Present day "normal" temperature gradients are about 1°C per 100 feet depth, and original depths of deposition of the ore minerals are generally considered to have been less than 5000 feet and thus, inclusion temperatures that exceed 60°C are anomalously high for present "normal" gradients (White 1968). According to Roedder (1967 a) who reviewed the data obtained by various workers on homogenization temperatures of fluid inclusions from Mississippi Valley ore deposits, the formational temperature would be between 100° and 150°C and very rarely as high as 200°C.

For comparison the Salton Sea Geothermal system shows temperatures near the center of the field as about 300°C at 3000 feet and 360°C at 7000 feet.

The two hot pools in the Red Sea Geothermal system are the Discovery Pool with a maximum temperature of 44.9°C , and the Atlantis II Pool with a temperature of 56°C at a depth of 2040 m (White 1968).

The temperature of natural systems are higher than the laboratory temperature maintained by Garber ($25^{\circ} \pm 2^{\circ}\text{C}$). Temperature does effect the pH which would change to acidic side with increasing temperature as calculated by Helgeson. Steger (1973) reported that the decrease in the sorption of metals with increasing acidity is due to the decrease in the dissociation of the sorption sites. Kipling (1965) states that for completely miscible systems, selective adsorption generally decreases with increasing temperature, as it is expected effect for an exothermic process, and it is compitable with a decrease in the magnitude, and hence in specificity of Van der Waal's forces as the temperature increases. Thus, adsorption by charcoal of acetic acid from aqueous solutions decreases as the temperature increases (Groves et al. 1947). For adsorption of solids from solution, with increase in temperature; the isotherm usually falls to lower levels, particularly at the lowest concentrations, though it may reach almost the same limiting value at high concentrations (Kipling 1965).

Sen and Guha (1963) have experimentally shown that on heating a kaolinite clay to 1000°C , its cation exchange capacity showed no change until 400°C . Above 400°C there was a sharp increase to about 550°C followed by a gradual decrease broken by a relatively more moderate decrease between 700° and 800°C . The increase in the cation exchange capacity is correlated with the disruption of the kaolinite structure on dehydroxylation. The subsequent decrease in capacity suggests reorganization in the resulting product.

From literature quoted above it can be concluded that adsorption

decreases at higher temperatures but, there is no change in adsorption at temperatures below 400°C as noted by Guha and Sen. Natural temperatures were between 100° to 150°C (Mississippi Valley). This temperature range is not high enough to affect the adsorption. Therefore, present laboratory experiments done at room temperatures can be related to the field conditions.

CHAPTER 8

CONCLUSIONS.

The conclusions of this study are summarized below:

1. A direct relationship exists between lead, zinc and copper sorption and the Al_2O_3 content of dolomites but not of limestones. However, there is a significant direct relation between copper sorption and Al_2O_3 content of the limestones, which is probably due to the exchange affinities between copper and calcium of the calcium rich clays in limestones. Metal sorption is a direct function of clay content of dolomites.
2. The inverse relationship found in dolomites between copper, lead and zinc sorption and MgO content is due to increase in MgO content which decreases the Al_2O_3 content and thereby decreases the metal sorption.
3. In limestones lack of correlation between lead and zinc sorption and CaO and MgO contents is attributed to chemisorption.
4. Lack of correlation between lead and zinc sorption and Al_2O_3 content in limestones is a function of chemisorption and not physical adsorption, since calcite can react with lead and zinc to form carbonates of lead and zinc. This masks the available surface area on the clay mineral and obscures physical adsorption.
5. The direct relationship between water sorption and limestones, and lack of correlation between lead and zinc sorption of limestones suggests that the limestones react with metal ions to form the corresponding metal carbonates and their concentration is not related to the internal surface area.
6. The correlation between water sorption and metal sorption of dolomites suggests that metals are concentrated by physical adsorption on dolomites.

7. Lack of correlation between CaO content of dolomites and metal sorption suggests that calcite in dolomite is reactive with metals and obscures physical adsorption.

In the Mississippi Valley type of deposits where no igneous source of mineralization is apparent, and the source of mineralizing solutions as well as the processes of mineralization, after many years of study are still enigmatic. It is interesting to note the similarities between such deposits and the observations made in this laboratory study. For example some of the geochemical characteristics of such deposits are:

1. The principal sulphide metals are lead and zinc. Copper is almost absent.
2. In any one area the sulphides tend to favour a particular facies- dolomite or limestone, in many instances dolomites are the preferred host rocks.
3. They are low temperature deposits (100° - 150° C).
4. The host rocks contain organic matter and some fluid inclusions contain petroleum.

It is therefore possible that adsorption may play a part in the concentration of metals ultimately leading to sulphide deposition in carbonate rocks.

The direct correlation between copper and alumina content of limestones and dolomites reveals that copper prefers alumina (clay). This suggests why copper is excluded from the carbonates and prefers shales (e.g. Kupferschiefer, Roan Province, Zambia etc.).

The direct relationship between Pb, Zn and Al_2O_3 content of dolomites indicates that argillaceous dolomites may be preferable host rocks (e.g. dolomitic shales of MacArthur River, Australia).

The typical association of lead-zinc deposits with limestones and dolomites can be explained as follows:

The lead and zinc present in the limestones is due to the chemisorption of these metals by calcite, since no correlation was seen between Pb, Zn, CaO and MgO contents in limestones.

The lead-zinc association with the dolomites reveals that dolomites are more surface active and less chemically reactive and adsorb metals by means of physical adsorption and may thus concentrate metals.

A relation was observed between Pb, Zn and Mg content of dolomites. In these deposits syngenetic dolomitization of limestones is probably a prerequisite in order to form a suitable host rock for metallization (e.g. dolomitic limestones of east Tennessee and Kazakhstan; and syngenetic dolomitization of the brecciated carbonate rocks and sulphide mineralization at northern Baffin Island).

The room temperature at which the experiments were performed suggests that the lead-zinc deposits can form at low temperatures as low as 25°C. Presence of organic matter in the host rocks enhances the metal sorption in a manner similar to clays by increasing the internal surface area.

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