The Effect of Dolomitization On the Strontium Concentration In the Columbus Limestone Columbus, Ohio

By

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Geology 570

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Introduction:

In the diagenesis of limestone into dolomite there are three things which can happen to the concentration of the element strontium. These are 1.) the strontium concentration may increase as the percent of dolomite increases, 2.) it may remain constant as the percent of dolomite increases or 3.) it may decrease as the percent of dolomite increases. At the outset of this experiment a working hypothesis was formed. This hypothesis was that as the percent of dolomite increases the concentration of strontium should decrease.

The reasoning behind this hypothesis was as follows. Strontium, calcium and magnesium have fairly similar atomic radii; magnesium 1.60 Å, calcium 1.97 Å and strontium 2.15 Å and the same oxidation states (+2). It is because of these similarities that strontium is capable of occupying the same lattice sites as the calcium in limestone as noted by Graf (1960). If the dolomite tested was formed by the replacement of magnesium for the calcium in the lattice sites then it is also possible that the strontium initially present would also be replaced by the magnesium. The same agent that brought in the magnesium and removed the calcium could, if the previous assumptions were true, also remove the strontium providing it did not bring in any more strontium. If this is true then the more calcium which is replaced by magnesium (the larger the percent of dolomite), the more strontium should also be replaced (the lower the concentration of strontium).

There are several assumptions made. One of these assumptions is that the concentration of strontium which was initially present in the limestone was, for the most part, constant throughout the total thickness of the formation sampled. The second assumption is that the greatest majority of the strontium initially present was in the calcium sites and not in accessory minerals such as celestite or strontianite.

Several tests would have to be run to determine the percent of dolomite and the concentration of strontium present in the limestone formation sampled. The results would then have to be evaluated to see if an inverse relationship did indeed exist between the percent of dolomite and the concentration of strontium or, if not, what ration is present.

The Columbus limestone:

The Columbus limestone was chosen to test. There were twenty five samples of the Columbus limestone taken from two different locations. The first fourteen specimens were taken from an outcrop along Mill Creek one mile from where Mill Creek enters the Scioto River. Mill Creek is located in Delaware County west of the town of Bellepoint, Ohio

The remaining eleven specimens were taken from an outcrop in Hayden Run. Hayden Run is in Franklin County north west of Columbus, Ohio. The outcrop is just south of Hayden Run Road and one mile west of Scioto River Road.

The section at Mill Creek is approximately fourty-five feet thick and is high in dolomite content. This section was sampled at approximately three feet intervals throughout it's entire thickness. The first specimen was taken just above a conglomerate bed, which marks the base of the Columbus limestone, and the last specimen at a bed containing colonial coral, probably a species of Stromatopora.

The section at Hayden Run is approximately sixty-five feet thick. In contrast to the Mill Creek outcrop, this section is almost entirely limestone, The Hayden Run outcrop was sampled at every major bed starting at the base of Hayden Run Falls where Stromatapora occurs, (this gives an approximate corralation between the two sections), to the top of the outcrop which is just below the base of the Delaware limestone. Although these two sections are seperated by approximately fifteen miles they include almost the total thickness of the Columbus limestone.

According to Stout (1941) the change in the dolomite content from very high in the lower part of the section to low in the upper part was to be expected. This is characteristic of the Columbus limestone and not a result of the seperation of the two outcrops. In addition to this it was also noted by Stout (1941) that the highly calcereous part of the section is much more fossiliferous then the section which is rich in magnesium.

Method:

In order to determine the effect of dolomitization on the concentration of strontium two tests had to be made on each sample. The first to determine the percent of dolomite by x-ray diffraction. The second to determine the concentration of strontium by x-ray fluorescence. Before these two tests could be run the specimens had to be prepared. The preparation was to grind each specimen, with a mortar and pestle, into a fine powder. The powder had to be fine enough to pass through a 140 mesh screen. After this was completed then the two x-ray tests could be run on the samples.

Percent of Dolomite:

The percent of dolomite present was determined by x-ray diffraction. The powdered sample was first mounted on a slide which was in turn mounted on a goniometer. The specimen was then exposed to x-radiation and rotated through an arc of from $25^{\circ}2\theta$ to $35^{\circ}2\theta$ and the x-radiation's counts per second were recorded on a chart. If any dolomite or calcite was present a seperate peak will appear for each in this ten degree arc. The calcite peak will come in at $29.4^{\circ}2\theta$ and the dolomite peak will come in at $31^{\circ}2\theta$. From these peaks it is possible to determine the percent of dolomite present. To find the percentage of dolomite the height of the calcite and dolomite peaks are measured and each is multiplied by the scale on which the test was run. This will give the amount of calcite and dolomite in counts per second. The dolomite concentration was then divided by the calcite concentration and the resulting figure is then used on the dolomite-calcite standardization curve to determine the percent of dolomite present in the sample assuming uniform dolomitization. The percent of calcite or limestone is found by subtracting the percent of dolomite from one hundred percent. In order to determine how accurate the readings were sample number eleven was tested ten times. From this data the limits of the readings were determined. The tests were run at 15 milliamperes and 45 KVP. The x-radiation was copper Kα which was passed through a nickel filter. The dolomite-calcite standardization curve was taken from Habib (1968). The results of this test are listed in Table 1.

Strontium Concentration:

The concentration of strontium in the sample was determined by x-ray fluorescence. The principle is similar to that used in the x-ray diffraction test. The powdered specimen was mounted on a goniometer and exposed to x-radiation while being run through an arc of from 23° 2θ to 27° 2θ. At 27° 2θ the goniometer was reversed and the specimen was run through the same are back down to 23° 2θ. As in the x-ray diffraction the counts per second of the x-radiation was recorded on a chart. Any strontium present

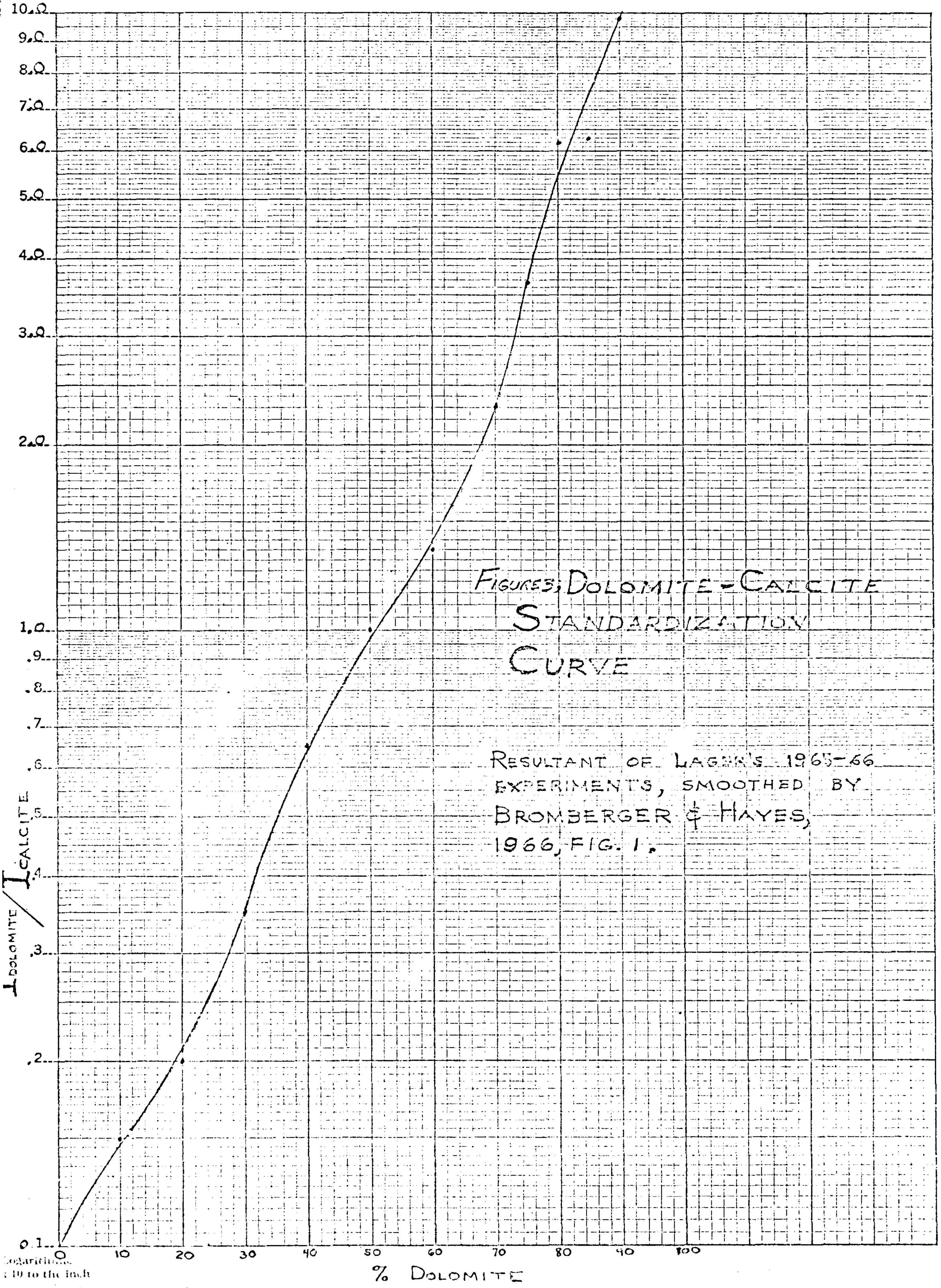
FIGURE 5; DOLOMITE - CALCITE
STANDARDIZATION
CURVE
RESULTANT OF LAGER'S 1965-66
EXPERIMENTS, SMOOTHED BY
BROMBERGER & HAYES,
1966, FIG. 1.
$I_{DOLOMITE}/I_{CALCITE}$
% DOLOMITE
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
.9
.8
.7
.6
.5
.4
.3
.2
0.1
0
10
20
30
40
50
60
70
80
90
100
Logarithmic
10 to the inch

Table 1. Percentage of dolomite and calcite

Sample	Concentration (CPS) Dolomite	Calcite	Dolomite/Calcite	Percentage ± 1.2 Dolomite	Calcite
1	1892	0	∝	100	0
2	1736	0	∝	100	0
3	1760	208	8.46	87.5	12.5
4	1732	228	7.61	85.5	14.5
5	1710	340	5.03	79	21
6	1954	0	∝	100	0
7	2120	110	19.3	100	0
8	1974	204	9.67	89.8	10.2
9	1970	48	41.1	100	0
10	1812	674	2.69	72	28
11	1622	588	2.76	72.2	27.8
12	2020	280	7.21	82.5	17.5
13	0	1964	0	0	100
14	0	1958	0	0	100
15	58	2176	0.027	0	100
16	710	1632	0.435	33	67
17	232	1700	0.136	7.8	92.2
18	188	1862	0.101	0	100
19	128	1738	0.074	0	100
20	186	1818	0.102	0.5	99.5
21	98	2062	0.047	0	100
22	156	1780	0.088	0	100
23	0	1788	0	0	100
24	0	1934	0	0	100
25	0	1816	0	0	100

Table 1. Percentage of dolomite and calcite

Sample	Concentration (CPS) Dolomite	Calcite	Dolomite/Calcite	Percentage ± 1.2 Dolomite	Calcite
11	1668	686	2.43	70.5	29.5
11	1606	606	2.65	72.0	28.0
11	1646	590	2.79	72.6	27.4
11	1658	570	2.90	72.9	27.1
11	1654	608	2.72	72.2	27.8
11	1656	570	2.91	72.9	27.1
11	1604	572	2.81	72.5	27.5
11	1660	604	2.75	72.3	27.7
11	1668	606	2.74	72.3	27.7
11	1660	622	2.67	72.0	28.0

would give a peak at 25.15 2θ. From the intensity of this peak the concentration of strontium could be determined. The first step was to measure the height of the strontium peak and multiply by the scale the test was run on. Since two peaks were obtained for each specimen because the arc was run through twice an average intensity for the strontium in counts per second could be obtained. The intensity of the strontium was then used on figure 5 to determine the concentration of strontium in parts per million. As in the x-ray diffraction test the accuracy of the data had to be checked. To determine this a standard limestone sample (#309) was tested four times. From this the limits of the strontium concentration can be determined. In addition to determining the limits of the strontium concentration sample 309 was also used to construct the strontium concentration curve. The tests were run at 55 milliamperes and 65 KVP. A lithium fluoride crystal was used with the Δ E in. The readings were taken on the K α x-radiation. The standard limestone sample (309) was obtained from Dr. Gunter Faure and the strontium concentration curve from Habib (1968). The results of the tests for strontium concentration are shown in Table 2.

Discussion:

From the data acquired from the two tests which were run on the samples it was possible to show grahically, figure B, the relationship between the percent of dolomite and the concentration of strontium. From this graphical

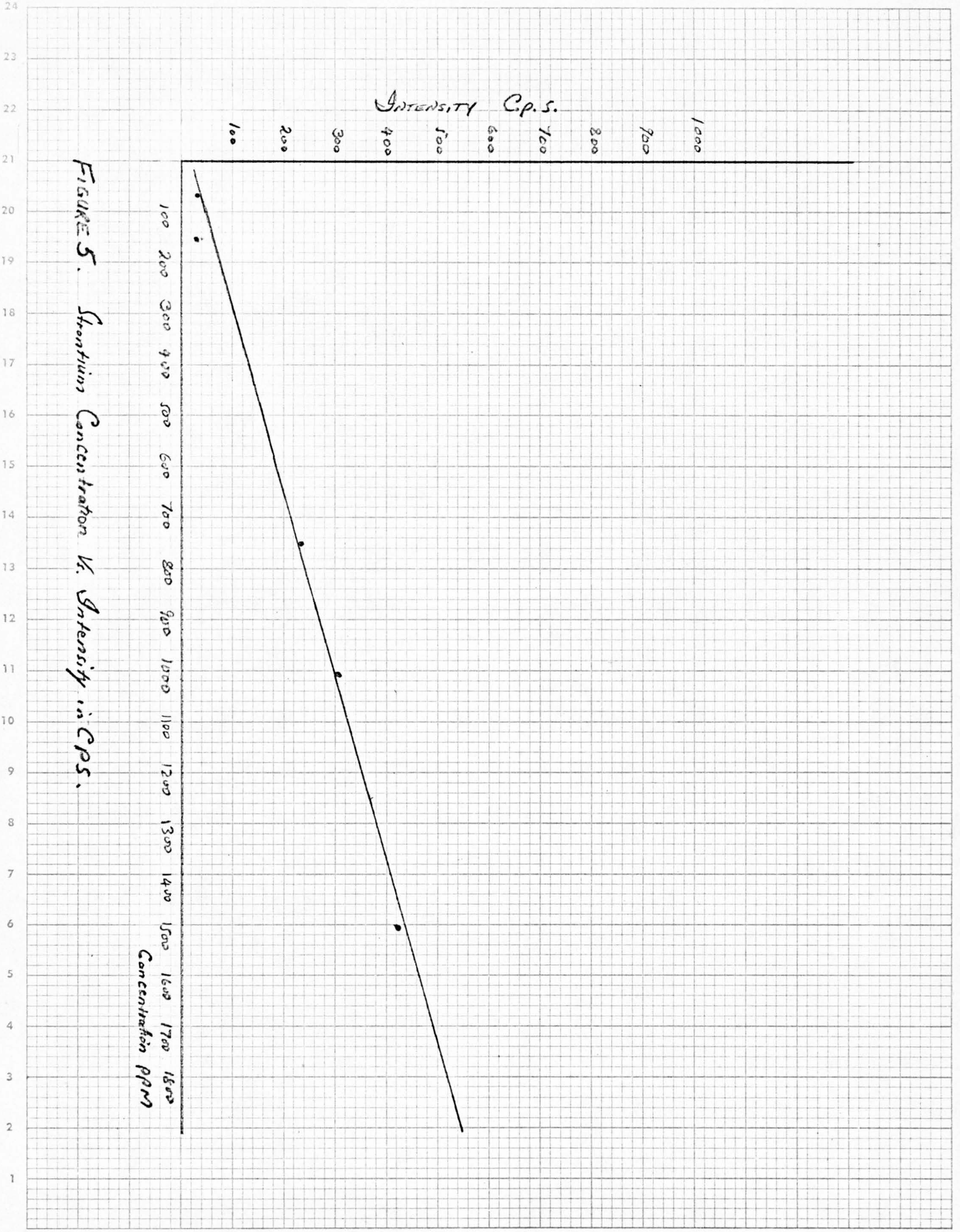

Figure 5. Strontium Concentration V. Intensity in CPS.

Table 2. Strontium concentration

Sample	Sr Concentration (inches)	Scale	Sr Concentration (CPS)	Sr Concentration (ppm) ± 270
309	6.025	5000	3012	8340
1	0.690	5000	345	1170
2	1.945	2000	389	1330
3	1.920	2000	384	1310
4	1.965	2000	393	1340
5	1.690	2000	338	1130
6	1.820	2000	365	1240
7	1.830	2000	367	1250
8	1.805	2000	361	1230
309	5.770	5000	2885	7800
309	5.945	5000	2972	8200
9	1.710	2000	342	1160
10	1.855	2000	371	1260
11	2.125	2000	425	1460
12	2.035	2000	407	1390
13	1.265	2000	253	840
14	1.920	2000	384	1310
15	2.185	2000	437	1500
16	2.155	2000	431	1480
17	3.950	2000	790	>1800
18	2.385	2000	477	1640
19	3.880	2000	776	>1800
20	1.830	2000	366	1240
21	1.930	2000	386	1320
22	2.160	2000	438	1500

Table 2. cont.

Sample	Sr Concentration (inches)	Scale	Sr Concentration (CPS)	Sr Concentration (ppm) ± 270
23	1.775	2000	355	1200
24	1.965	2000	393	1350
25	2.235	2000	447	1540
309	5.800	5000	2900	8020

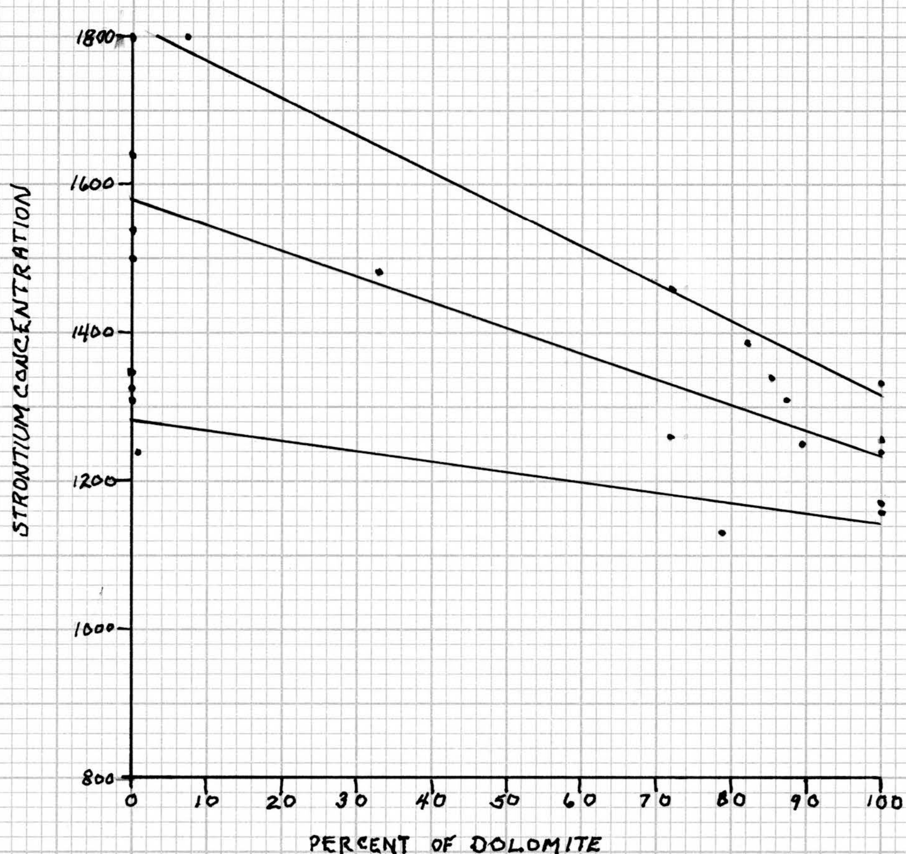
STRONTIUM CONCENTRATION
1800
1600
1400
1200
1000
800
0
10
20
30
40
50
60
70
80
90
100
PERCENT OF DOLOMITE

FIGURE B

representation (the samples from the upper part of the formation are on the left of the graph) it appears that the hypothesis which stated that the strontium concentration might decrease as the percent of dolomite increased may be correct however before making a final judgement as to whether the working hypothesis is correct or not it will be necessary to consider several other factors.

The first of these factors to be considered are the accessory minerals which contain strontium such as celestite and strontianite. There are several ways in which these accessory minerals could effect the concentration of strontium in limestone and dolomite. One way would be if large amounts of these accessory minerals were initially present in the limestone. If this were the case then the dolomitization of the limestone would have no effect on the concentration of strontium. This possibility is very small since Graf (1960) found that most celestite is due to secondary redistribution. This however brings another problem to light, that of the secondary formation of accessory minerals. Even if most of the strontium was initially in the calcium sites the accessory minerals could still effect the strontium concentration. This is because the agent which brought in the magnesium did not remove all of the strontium which was removed from the calcium sites and this strontium formed the accessoryy minerals. These accessory minerals would now be in the dolomite even though they were not initially present in the limestone. If this were the case then the concentration of strontium would not decrease as the percent of dolomite increased. In the specimens tested the strontium concentration decreased and therefore the accessory minerals, in this instance, involving the strontium concentration were not formed.

Another source of strontium to be considered is that which is found in fossils. Strontium is found in modern clams and snails and therefore could also be present in the fossils which are found in the Columbus limestone. The concentration of strontium in the fossils are thought to be controlled by several factors. Graf (1960) seemed to think that the strontium content was dependant on the different genera while Kulp et al (1952) felt that the strontium content was a factor of the original strontium concentration in the water which is in turn controlled by the salinity of that water. It will be remembered that the Columbus limestone is much more fossiliferous in the upper sixty-five feet than in the lower fourty feet. The strontium content is also higher in the Hayden Run section which corresponds to the upper sixty-five feet of the Columbus limestone. The fact that the Hayden Run section is more fossiliferous could account for the greater concentration of strontium rather then the dilution by dolomitization of limestone but until more is known about the salinity of the water during the deposition of the Columbus limestone and the strontium present in the fossils it cannot be said which plays the most important part in the variation of strontium concentration.

Another factor to be considered in the decrease in strontium concentration is a stratigraphic one. It is possible that there is some type of unconformity present in the Columbus limestone which could cause the decrease in strontium from the lower to the upper part of the section rather than the increase in dolomitization. In order to establish whether this is true more research must be done on the environment of deposition of the Columbus limestone.

Conclusion:

Although figure B would seem to indicate that the hypothesis concerning a decrease in strontium with an increase in dolomite is correct a positive statement of it's validity cannot be made at this time. In order to make such a statement further analysis would have to be run on the samples. The content of strontium in the fossils would have to be studied to see if they played a significant role in the decreasing strontium concentration which was observed for the Columbus limestone. It may also be necessary to study the role the accessory minerals play in the strontium concentration.and also to determine if stratigraphy plays a part in the decreasing strontium concentration. Although the dolomitization of the limestone cannot be proven to be the sole reason for the decrease in the strontium concentration it cannot be ruled out without further study. It may in fact, after the other factors are studied, turn out to be the primary cause for the change in the strontium concentration in the Columbus limestone.

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