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Can Chromatography Occur in Nature?

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Can Chromatography Occur in Nature?

PAUL J. KEMP AND HARVEY DIEHL

Abstract. Adsorption of calcium and magnesium on a sandstone from a bicarbonate solution has been demonstrated. On elution with water saturated with carbon dioxide, the magnesium passes off first. The chromatographic separation of magnesium from calcium can thus occur under conditions which can prevail in nature.

We ask: Does chromatography play a part in geochemistry? More specifically we ask: Can calcium and magnesium be separated by the chromatographic process on sandstone? Even more specifically: Can such a separation be demonstrated in the laboratory on a natural sandstone under conditions which can occur in nature? The answers to all three questions appear to be yes.

For the demonstration we selected sandstone from the Chugwater and Tensleep formations of north central Wyoming. A

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solution containing calcium and magnesium bicarbonates was passed through the sandstone and the adsorbed calcium and magnesium eluted with water containing dissolved carbon dioxide. Suitable chemical analyses were made to show that calcium and magnesium were adsorbed and subsequently eluted and that differences exist in the behavior of calcium and magnesium during adsorption and elution, that calcium is the more firmly held to the sandstone. Greatest success was achieved with crushed Tensleep sandstone. Given an extended time to accommodate the slow percolation of water through the uncrushed sandstone, quite conceivably the same behavior and separation could occur under circumstances which may very easily prevail in nature.

EXPERIMENTAL WORK

Chugwater Sandstone. Slabs of Chugwater sandstone were obtained from the cliff immediately south of the Iowa State University Geology Camp on Shell Creek three miles east of Shell, Wyoming. Core drillings were also obtained from the Torchlight Oil Field, Basin, Wyoming.

Microscopic examination reveals that the Chugwater sandstone is extremely fine-grained and is composed of discrete pieces of quartz to which are attached discrete particles of hematite, the individual pieces being cemented together with carbonate. A chemical analysis of the Shell Creek sample indicated about 7 per cent of calcium oxide and 4 per cent magnesium oxide. The carbonate appears thus to be dolomitic in character.

Tensleep Sandstone. The Tensleep sandstone used was a well core from the Torchlight Oil Field, Basin, Wyoming. The stone was a light yellow-tan in color, of medium grain, highly porous, and quite friable. It contained a petroleum residue. Microscopic examination showed that the stone was composed of discrete, rounded particles of quartz, joined quartz to quartz, and a very small amount of pyroxene.

A sample of this sandstone was subjected to gentle grinding and a sieve analysis made on the residue:

Collected on Mesh	Particle diameter microns	Relative Quantity Per Cent
80	177 plus	2
100	177 - 149	3
115	149 - 125	6
150	125 - 105	46
200	105 - 74	30
270	74 - 53	6
pan	53 minus	7

Enough sandstone was ground to give approximately 500 g.

which passed 115 mesh and collected on a 150 mesh sieve. This material was washed five times with benzene and three times with acetone, the last washing in each case being made with reagent grade solvent. The material was air dried and then dried in an oven at 110° overnight. This material was then mixed for 30 minutes in a stainless steel V-type blender.

A chemical analysis of the crushed, mixed and sieved stone, 115-150 mesh, oven-dried, was analyzed in the following manner. Silica was determined by perchloric acid dehydration and correction of the impure silica with hydrofluoric acid and sulfuric acid. Iron, aluminum, calcium and magnesium were determined on aliquots of the filtrate from the silica determination. Iron was determined colorimetrically with 1, 10-phenanthroline. Iron plus aluminum was determined by an EDTA titration; an excess of EDTA was added, the solution was boiled for 5 minutes, boiling acetone was added until the turbidity which first formed was redissolved (about 60 per cent acetone total), the pH was adjusted with 35 per cent sodium acetate to 3.3 to 3.4, a saturated solution of diphenylthiocarbazone in 95 per cent ethanol indicator was added, and the excess EDTA titrated with standard zinc solution. Aluminum was then obtained by difference. Calcium and magnesium were determined by EDTA titrations, the former at pH 12.5 using Calcein as indicator, and the latter at pH 10 using Calmagite indicator. Carbon dioxide was determined on a separate sample (5 gm.) by gas evolution and absorption in ascarite.

Composition of Tensleep Sandstone	
Analysis of 115-150 mesh fraction; oven dried at 110°	
Silica	96.96 per cent SiO ₂
Iron	0.14 per cent Fe ₂ O ₃
Aluminum	0.20 per cent Al ₂ O ₃
Calcium	0.07 per cent CaO
Magnesium	2.63 per cent MgO
Carbon dioxide	0.09 per cent CO ₂
Total	100.09

No manganese could be detected by the periodate test.

A further test was made by leaching samples with an alkaline solution of EDTA for 24 hours. Some calcium and magnesium were removed:

	As Per Cent of the Sandstone	As Per Cent of the (Oxide Present)
Magnesium, as MgO	0.08	3.04 (of 2.63)
Calcium, as CaO	0.01	14 (of 0.07)

This is in agreement with the chemical analysis indicating that little carbonate is present and that the magnesium is present as silicate, presumably pyroxene.

Thermogravimetric analysis showed weight losses at 500-580°, 750-840°, 960-990° and 1045-1070°. The second and third weight losses totaled 0.09 per cent of the sample, equal to the amount of carbon dioxide as determined by chemical analysis.

Preliminary Experiments with Chugwater Sandstone. The Chugwater sandstone proved too impermeable to permit more than a barely detectable flow of water through cylinders 12 mm in diameter obtained by core-drilling the specimens. Flow of water through a column of the crushed sandstone was satisfactory at the beginning but dropped off to insignificant values as the experiments progressed. Flow was increased by raising the water head repeatedly but even with a head of 15 meters on a column specially designed to withstand the pressure, flow fell to such a low value as to make the experiment unmanageable.

The first step in the experiment was to remove the naturally occurring calcium and magnesium from the stone by leaching with water containing carbon dioxide. As the removal of the carbonate matrix progressed the very fine particles of quartz and hematite released settled and compacted, ultimately so tightly as to completely inhibit flow. Some results on the adsorption of calcium and magnesium on this fine residue and subsequent leaching with water bearing carbon dioxide indicated that a separation of magnesium from calcium was occurring, but the results were being won at such a high cost in time that the work was abandoned before really convincing evidence could be obtained.

Preparation of Column of Tensleep Sandstone. The 115-150 mesh portion of the Tensleep sandstone prepared as described above was placed in a vertical, glass tube, 1.7 cm. i.d., the 352 g. taken having a wet volume of 190 ml. and a height in the tube of 112 cm. A 2-m. head of water under 2 atmospheres pressure produced a flow of 17 ml. per minute when unrestricted. During unrestricted flow gas bubbles were formed from the carbon dioxide and air dissolved in the water and these disrupted the even flow. This effect was eliminated by keeping the entire column under essentially the same pressure by cutting the flow rate to 6.7 ml. per minute by means of a screw clamp on the outlet at the bottom.

Elution Reagents. Water and Water Saturated with Carbon Dioxide. Distilled water was deionized by passage through Amberlite MB3 and collected in a 10-liter Pyrex jug. Air rendered free of carbon dioxide by passage through Ascarite was bubbled through a fritted-glass diffuser and through the water to remove dissolved carbon dioxide.

Deionized water in a second 10-liter Pyrex jug was saturated with carbon dioxide by the direct addition of solid carbon dioxide. Excess carbon dioxide was allowed to escape around the stopper of the jug by varying the pressure on the stopper so as to maintain a pressure of two atmospheres inside the jug.

Both jugs were connected to the laboratory air line through a pressure reduction valve with attached gauges. This air was used to maintain the gas pressure within the jugs at 2 atmospheres as liquid was removed through siphon tubes. The jugs and sandstone column were connected with plastic tubing to minimize contact with glass and reduce pickup of calcium and arrangement was made to draw liquid from either jug as desired.

In preparing these solutions precautions were observed to avoid the introduction of calcium and magnesium from dust and tobacco smoke. It was necessary to crush the dry ice in a clean sheet of polyethylene inasmuch as cloth towels and paper when used contaminated the dry ice with calcium and magnesium, presumably from residue left from hard water used in their washing or manufacture.

Magnesium Bicarbonate Solution. A weighed amount of magnesium metal (assay 99.3 per cent magnesium) was dissolved in exactly 1 liter of deionized water by passing carbon dioxide through the mixture until all of the magnesium had dissolved. This solution was stable during the period of the experiment. Just prior to use, portions of this solution were placed in a flask and suction applied to the flask for 15 minutes to remove the excess carbon dioxide; a measured volume of the solution was then transferred to the sandstone column.

Calcium Bicarbonate Solution. Carbon dioxide was bubbled for 15 days through a suspension of reagent grade calcium oxide in water. The calcium oxide was allowed to settle and the concentration of the calcium in the clear solution was determined by chemical analysis. This solution was stable for only a few hours unless carbon dioxide was bubbled continually through it. Just prior to use, portions of this solution were placed in a flask and suction applied to the flask for 15 minutes to remove excess carbon dioxide.

Analytical Methods. Because of the very small amounts of calcium and magnesium in the various portions of the eluate, fluorometric methods were used for the determination of both calcium and magnesium. Magnesium was determined with the o,o'-dihydroxyazobenzene reagent of Diehl, Olsen, Spielholtz and Jensen (1). Calcium was determined with the Calcein reagent of Diehl and Ellingboe (2) as developed by Phillips (3).

Both methods are described in the monograph by Diehl (4). In both determinations the final solutions for measurement, prepared in disposable plastic cuvetts, were immersed in a constant temperature bath for 15 minutes and the measurement of fluorescence intensity made expeditiously after removal from the bath. Intensity measurements were made with a G. K. Turner Associates Model 110 Fluorometer.

Calibration curves were prepared using standard solutions prepared from primary standard magnesium iodate tetrahydrate and primary standard calcium carbonate. The calibration curve for magnesium covered the range zero to 25 $\mu\text{g.}$ of magnesium per 50 ml. and was linear over the entire range. The curve for calcium covered the range zero to 5 $\mu\text{g.}$ of calcium per 5 ml.; the curve was linear up to 1.3 $\mu\text{g.}$ and slightly convex upward beyond.

Experiments with Tensleep Sandstone. Preliminary experiments were made with small columns of the 115-150 mesh sandstone to establish working values for the concentration ranges and to test the analytical procedures. These preliminary experiments indicated that the original magnesium in the sandstone could be removed with water saturated with carbon dioxide, and that magnesium was then adsorbed on the sandstone from a solution of magnesium bicarbonate and subsequently eluted with water saturated with carbon dioxide.

The column of sandstone described above was then prepared. Four experiments were performed on this column:

- 1) Water saturated with carbon dioxide was passed through the column to strip off any carbonic acid-soluble magnesium and calcium originally present in the sandstone. Carbon dioxide-free water was then passed through the column.

- 2) A measured volume of calcium bicarbonate solution, freed of excess carbon dioxide, was added to the top of the column, carbon dioxide-free water was passed through the column, and the adsorbed calcium was then eluted by the passage of water saturated with carbon dioxide. The eluate was collected in successive 100-ml. portions and each portion was analyzed for calcium.

- 3) A measured volume of magnesium bicarbonate solution, freed of excess carbon dioxide was added to the top of the column, carbon dioxide-free water was passed through the column, and the adsorbed magnesium was then eluted by the passage of water saturated with carbon dioxide. Successive 100-ml. portions of the eluate were collected and analyzed for magnesium and for calcium.

- 4) A mixture of measured volumes of calcium bicarbonate and

magnesium bicarbonate solutions, freed of excess carbon dioxide, was added to the top of the column and carbon dioxide-free water was passed through the column. The adsorbed calcium and magnesium were then eluted with water saturated with carbon dioxide. Successive 100-ml. portions of eluate were collected and each analyzed for calcium and magnesium.

RESULTS

In experiment 1), the initial leaching to remove the carbonic acid-soluble calcium and magnesium naturally present in the sandstone, 30 liters of water saturated with carbon dioxide were passed through the column. Analysis of random samples of the eluate showed that calcium and magnesium were being removed from the sandstone. Analysis of the final portions of the eluate revealed almost no calcium or magnesium in the effluent samples, indicating that the removal of the soluble calcium and magnesium was essentially complete.

In experiment 2), 100.1 mg. of calcium was introduced. Not all of the calcium was adsorbed, for calcium amounting to 33.24 mg. was found in the effluent of the carbon dioxide-free water used to wash the sample into the column. This indicated that 66.86 mg. of calcium had been adsorbed. This adsorbed calcium was eluted with water saturated with carbon dioxide, the analyses of the successive portions of the eluate giving a typical elution curve (Figure 1). The calcium eluted totaled 28.28 mg.

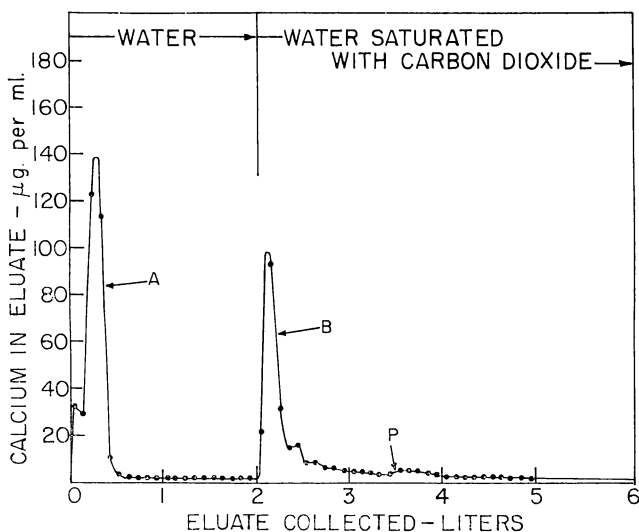


Figure 1. Adsorption and elution of calcium on Tensleep sandstone. A. Excess calcium passing through column; B. Adsorbed calcium eluted by water saturated with carbon dioxide; p. Elution stopped for 13 hours

bringing the total calcium in the eluate to 61.5 mg. Thus, some 34 to 38 mg. of calcium remain unaccounted for, presumably owing to retention of calcium on the sandstone although the accumulation of analytical errors may account for a few milligrams.

In experiment 3), 100.2 mg. of magnesium was added. The effluent from the carbon dioxide-free water used to wash the sample into the sandstone contained 49.8 mg. of magnesium, indicating that 50.44 mg. of magnesium had been adsorbed on the sandstone. This adsorbed magnesium was eluted with water saturated with carbon dioxide, a typical elution curve

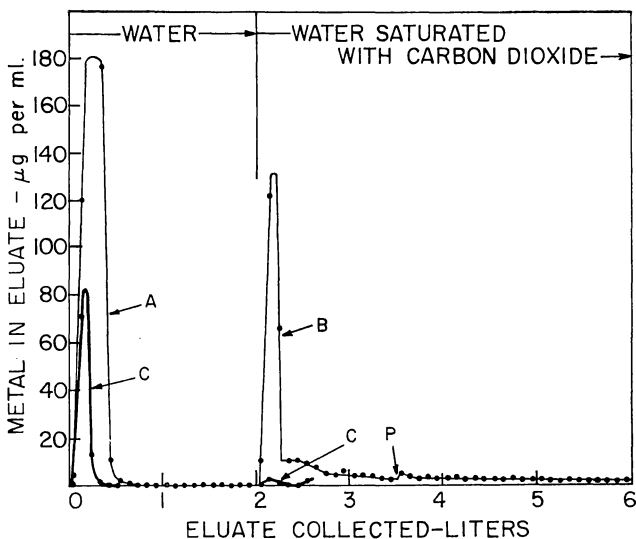


Figure 2. Adsorption and elution of magnesium on Tensleep sandstone. A. Excess magnesium passing through column; B. Adsorbed magnesium eluted by water saturated with carbon dioxide; C. Calcium (from previous experiment) displaced by magnesium; p. Elution interrupted for 18 hours

resulting (Figure 2). The eluted magnesium totaled 31.6 mg., bringing the total magnesium in the eluate to 81.4 mg. Thus, 18.8 mg. of magnesium were unaccounted, this magnesium presumably remaining on the column.

In experiment 4), 10.00 mg. of calcium and 10.02 mg. of magnesium were added. Practically all of each metal was adsorbed, the eluate from the water wash containing 0.173 mg. of calcium and 0.694 mg. of magnesium; that is, 9.827 mg. of calcium and 9.326 mg. of magnesium were adsorbed. The adsorbed magnesium again gave a typical elution curve when eluted with water saturated with carbon dioxide, but the elution of the

calcium was delayed until most of the magnesium had been removed (Figure 3). The calcium in the eluate totaled 5.08 mg.; the magnesium eluted totaled 13.65 mg. The total calcium in

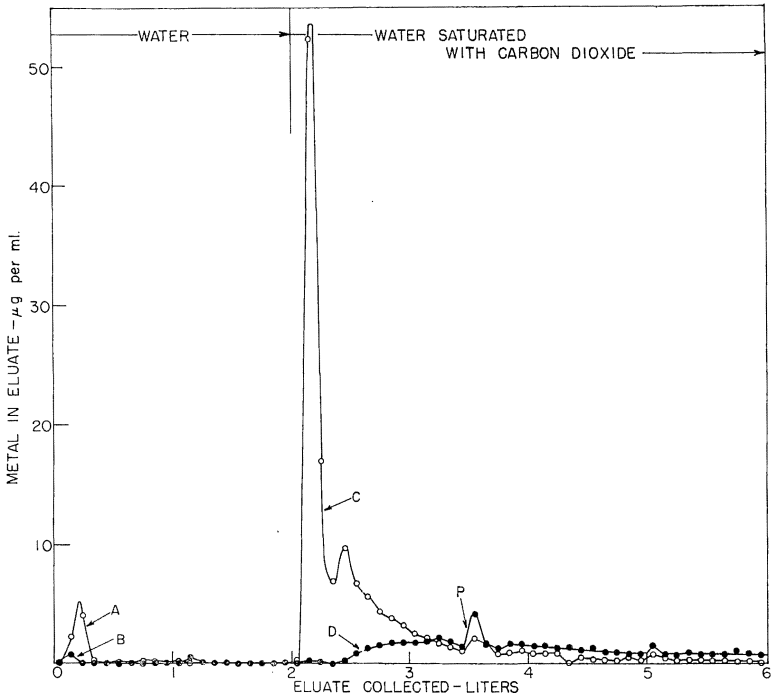


Figure 3. Adsorption and elution of calcium plus magnesium on Tensleep sandstone. A and B. Magnesium and calcium, respectively, not adsorbed during passage of wash water; C and D. Adsorbed magnesium and calcium, respectively, eluted with water saturated with carbon dioxide; p. Elution interrupted for 13 hours

the eluate (from water wash and water saturated with carbonic dioxide) was 5.26 mg.; and the magnesium 14.34 mg.

During the adsorption of magnesium in experiment 3, 8.99 mg. of calcium were collected in the effluent from the carbon dioxide-free water (Figure 2) used to wash the magnesium sample into the column, indicating that the high concentration of magnesium displaced the adsorbed calcium remaining on the column from experiment 2. Not all of the magnesium was eluted in experiment 3 and this accounts for the magnesium in excess of 100 per cent recovered in experiment 4. Some calcium still remained on the column after the elution with water saturated with carbonic acid in experiment 4.

The data obtained from experiments 2 and 3 are summarized in Table 1, that from experiment 4 in Table 2.

Table 1. Adsorption and Elution of Calcium Alone and Magnesium Alone on Tensleep Sandstone

	Calcium (Experiment 2)		Magnesium (Experiment 3)	
	mg.	Per Cent	mg.	Per Cent
Total metal added	100.1	100.0	100.2	100.0
Metal not adsorbed	33.2	33.2	49.8	49.7
Metal adsorbed	66.9	66.8	50.5	50.4
Metal eluted	28.3	28.3	31.6	31.5
Total metal in eluate	61.5	61.5	81.4	81.2

Table 2. Adsorption and Elution of Calcium Plus Magnesium on Tensleep Sandstone (Experiment 4)

	Calcium		Magnesium	
	mg.	Per Cent	mg.	Per Cent
Total metal added	10.00	100.0	10.02	100.0
Metal not adsorbed	0.173	1.7	0.694	6.9
Metal adsorbed	9.82	98.2	9.33	93.1
Metal eluted	5.08	50.8	13.65	136
Total metal in eluate	5.26	52.6	14.34	143

DISCUSSION

Had it been possible to maintain flow through the Chugwater sandstone, it is quite likely that the amounts of calcium and magnesium adsorbed would have been greater than those observed for the Tensleep sandstone because of the larger surface of the smaller particles.

Experiments 2) and 3) with the Tensleep sandstone, in which excess of calcium and magnesium, respectively, were passed through the column, yield a measure of the adsorption capacity of the sandstone: 0.190 mg. (4.75 μ moles) of calcium and 0.143 mg. (5.89 μ moles) of magnesium per gram of sandstone. A calculation of the amount of calcium which can be adsorbed as a monomolecular layer on one gram of sandstone, assuming spherical particles of diameter 115 microns and using 2.65 for the density (of quartz) and 0.99 A for the radius of the calcium ion, gives 0.83 μ moles. The observed value is some 5.7 times greater indicating a greater surface area and some porosity of the individual particles. The corresponding figures for magnesium (ionic radius 0.65 A) are 1.96 μ moles of magnesium per gram of sandstone and 3.0 for the ratio of observed to calculated.

A greater capacity of the sandstone for magnesium (on a molar basis) is expected because of the smaller ionic radius and this was found experimentally. Calcium, however, is more strongly adsorbed than magnesium and the magnesium passes off first during elution. Although more firmly held, adsorbed calcium is displaced by mass action by magnesium when the concentration of the latter is sufficiently great.

Admittedly it would have been better for our thesis that chromatography can occur in nature had the sandstone not been changed physically. However, the grinding was mild in action, hardly more than pressure from the fingers, and just sufficient

to break the matrix without crushing the individual particles. This did permit removing the exceptionally fine portion and made possible a flow rate reasonable for laboratory work in a finite time. New surface was undoubtedly exposed at the fractures but it is reasonable to presume that this merely increased the total surface without changing its character.

Water saturated with carbon dioxide at two atmospheres pressure will occur naturally only under unusual circumstances. At the lower partial pressure of carbon dioxide in the atmosphere, less carbon dioxide is present and the pH higher, about 5.8 in contrast to 4.0 for our water saturated with carbon dioxide at two atmospheres. We picture the separation of magnesium from calcium as resulting from continually repeated exchange adsorption of magnesium and calcium during passages over the sandstone and regard the carbonic acid-bicarbonate system essentially as a carrier supplying a suitable anion. The process should operate at any pH range in the carbonic acid-bicarbonate buffer region. The efficiency of the process may well depend on the carbon dioxide pressure and thus on the pH, but we have not examined this.

SUMMARY

Adsorption of calcium and magnesium on a sandstone from a bicarbonate solution has been shown. On elution with water saturated with carbon dioxide, the magnesium passes off first. A chromatographic separation of magnesium from calcium has thus been demonstrated under conditions which can occur in nature.

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