Arkansas Water
Resources Center

TRACE METAL AND MAJOR ELEMENTS IN WATER-SOLUBLE ROCKS OF NORTHWEST ARKANSAS

PREPARED BY:

George H. Wagner, Kenneth F. Steele and Doy L. Zachry, Jr.

PUB-036

October 1975

ARKANSAS WATER RESOURCES
UNIVERSITY OF ARKANSAS
112 OZARK HALL
FAYETTEVILLE, ARKANSAS 72701

TRACE METALS AND MAJOR ELEMENTS IN WATER-SOLUBLE ROCKS OF NORTHWEST ARKANSAS

by

George H. Wagner, Kenneth F. Steele and Doy L. Zachry, Jr.

ARKANSAS WATER RESOURCES RESEARCH CENTER

Publication No. 36

October, 1975

Trace Metals and Major Elements in Water-Soluble Rocks of Northwest Arkansas

Trace Metals and Major Elements in Water-Soluble Rocks of Northwest Arkansas

George H. Wagner, Kenneth F. Steele and Doy L. Zachry Jr.,
Department of Geology, University of Arkansas, Fayetteville, 72701

ABSTRACT

Trace metals in limestone are potential water contaminants because they can enter the ground water when the limestone is dissolved by carbonic acid and other naturally occurring acids. Four local limestones, the St. Joe and Pitkin Formations (Mississippian) and the Brentwood and Kessler Members of the Bloyd Formation (Pennsylvanian) were sampled in a five county area in Northwest Arkansas. Atomic absorption analyses were made for Na, K, Mg, Ca, Zn, Cu, Ba, Fe, Co, Cr, Ni, Mn, Li and Sr on the acid soluble material of the samples. All the limestones are relatively pure $CaCO_3$ with Pitkin the purest, 93.4%. Calcium and acid soluble material values varied only 3-5% from the average among the limestones whereas 71-108% variation occurred for Fe, Mn, K and Cr. Other elements showed intermediate variations. Only Fe and Mn are present on the average in the limestones at concentration levels which might lead to contamination of ground water to undesirably high levels. Analyses compare well with the reported "average" limestone except for acid insoluble elements which were not dissolved in our scheme and lithium (1.5 ppm average vs 20 in reference). Ratios of Sr/Ca and Mg/Ca were similar to reported values for limestones of comparable geologic age. Maxima in the areal variation of these ratios occurred at about the same latitude for three of the formations. The areal variation of Fe/Ca and Mn/Ca was also determined for the four limestone formations.

Interelement correlations in the limestones showed: Na, Sr, Li, Fe and Zn contents increased with Mg content; Mn and Cr increased with Fe content. Indications were obtained that detrital and other materials not in the calcite structure can be determined by their relative insolubility in acetic acid compared to hydrochloric acid.

Trace Metals and Major Elements in Water-Soluble Rocks of Northwest Arkansas

George H. Wagner, Kenneth F. Steele and Doy L. Zachry Jr.,
Department of Geology, University of Arkansas, Fayetteville, AR 72701

Introduction

In previous reports (Wagner and Holloway, 1974; Wagner, 1975) the elemental content of local rain water, including trace metals was given. The present report is concerned with another potential source of trace metals, the local water-soluble rocks. Data from both sources, rain water and limestones, are being used in a report now in progress to explain the elemental composition of local ground water.

Potential sources of trace metals in ground water must include the water soluble rocks such as limestone and dolomite. These two are the principal water-soluble rocks for Northwest Arkansas because other candidates such as evaporites, gypsum and halite, are missing and the silicates such as chert are less soluble. Both limestone and dolomite are rather insoluble in water by themselves.* However, as illustrated below for limestone (ls), the rocks are dissolved by the CO_2 of the air which dissolves in water to make carbonic acid (H_2CO_3), a weak acid.

---

*Comparative water solubility data are given below.

			Solubility	ppm of Ca^{++} at Saturation(25°C)	
Rock	Mineral	Formula	Product(25°C)	no CO_2 added	atmospheric CO_2
limestone	calcite	$CaCO_3$	$10^{-8.35}$	5.4	20
dolomite	dolomite	$CaMg(CO_3)_2$	10^{-17}	<<5.4	$\sim$20
gypsum	gypsum	$CaSO_4.2H_2O$	$10^{-4.62}$	600	600

$$CO_2 + H_2O = H_2CO_3 \qquad (1)$$

$$H_2CO_3 = H^+ + HCO_3^- \qquad (2)$$

$$CaCO_3(ls) + H^+ = Ca^{++} + HCO_3^- \qquad (3)$$

The air contains only .03% CO_2 and in spite of good equilibration with water atmospheric CO_2 would only bring the calcium content to about 20 ppm in water. Ground water frequently contains 40 ppm or more of calcium. This is attributed to plant respiration and decay of organic matter which can cause soil air to contain many times as much CO_2 as the air above ground (see p. 136 of Hem, 1970). The soil also contains organic acids which can dissolve limestone. Magnesium, either from dolomite, or as a substitute ion for calcium in limestone dissolves by similar mechanisms. Calcium and magnesium which together make up almost all the hardness of water, originate in the water-soluble rocks and find their way into water as illustrated above. The same pathway should be followed by trace metals and other ions which substitute for calcium or magnesium in limestone or dolomite.

Magnesium, up to about 5 mol percent, can substitute for calcium in calcite, the limestone mineral. It is expected that heavy metals in trace amounts, less than 1%, can do the same. Strontium, iron, barium, zinc, and other divalent ions which form carbonate minerals should form solid solutions in calcite of 1% or less. See pages 7-9 of Graf (1960) for a more detailed discussion. Monovalent ions such as sodium and potassium may do the same. Furthermore, any of the trace elements could occur as interstitial or occluded minerals in limestone. Many minerals such as pyrite, clays, etc. can form in the limestone by authigenic and diagenetic processes or occur as detrital material. All the trace elements listed above and others have been found in carbonate rock (Wolf, et. al., 1967).

Dissolution of limestone by carbon dioxide as illustrated by equations (1) to (3), and by natural organic acids or by a strong acid such as sulfuric acid from oxidation of pyrite, would be expected to librate the trace elements. By such dissolution the trace elements become potential pollutants for ground water. The extent to which the elements actually dissolve in the water is a function of the acidity (pH) and oxidation potential (Eh) of the solution and the solubility product of the chemical species involved. The trace element content of the water-soluble rocks thus measures potential water pollution.

A generalized stratigraphic column for the Pennsylvanian and Mississippian age rocks of Northwest Arkansas is shown in Figure 1. There are five limestone formations which, proceeding from youngest to oldest are: Kessler, Brentwood, Pitkin, Hindsville*and St. Joe. This report is concerned with the elemental analyses of all of these except the Hindsville. Dolomite rocks are much older (Ordovician), are at much greater depths in Northwest Arkansas and become exposed only in northcentral Arkansas. In addition to the limestone formations mentioned above the Prairie Grove and Boone Formations shown in Figure 1 can be highly calcareous. The Boone Formation is the aquifer most used for wells in the rural areas of Northwest Arkansas.

Figure 2 shows the sampling locations for the limestones used in this report. As shown in the following summary, 65 samples from 25 locations were analyzed.

---

* Member of Batesville Formation

Limestone	Number of Locations Sampled	Total Number of Samples Analyzed
Kessler	4	8
Brentwood	10	18
Pitkin	4	18
St. Joe	7	21
Grand Total	25	65

Analyses were made by dissolving the samples in acid and analyzing the acid soluble portion by atomic absorption for the following 14 elements: Na, K, Mg, Ca, Zn, Cu, Ba, Fe, Co, Cr, Ni, Mn, Li and Sr. Calcium is the most concentrated element and because of the high calcite ($CaCO_3$) content most of the samples approach the theoretical maximum of 40% calcium. Magnesium and iron are usually the next most abundant elements, occurring up to a few percent, followed by manganese which is in the tenths of a percent range in several samples. Other elements are in the 0.0X% (X00 ppm) range or less.

As pointed out earlier, trace metals can originate from substitution in the calcite structure or from diagenetically formed minerals outside the structure. The analyses do not differentiate as to which of these is the source of the trace metals. However, by comparing the metals dissolved by a weak acid (acetic) with those dissolved by hydrochloric acid, indications were obtained that iron and other trace heavy metals, except manganese, are predominantly from interstitial sources. Magnesium can come from both sources and Mn, Na, K, Li, Sr and Ba come primarily from the structure. Whether the interstitial material was formed by remobilizing of the limestone or from foreign sources is not known.

Interrelationship of the various elements in the limestones are examined in this report. Correlation of the atomic ratios with age of the rocks and with determinations by other workers on other limestones is also examined. The areal variation of the concentration of various elements in the limestones is depicted and discussed with relation to their depositional setting. Implications of the results to the water chemistry of the area are given.

Experimental

All Kessler samples were supplied by Mr. John G. Williams and the samples are further described in his M.S. thesis (Williams, 1975). Brentwood samples were collected by one of us (Zachry). Eight of the Pitkin limestone samples correspond to those in Bennett (1965), while the remaining 10 were field collected by the authors from known Pitkin localities. Samples of St. Joe limestone were supplied by Mr. John D. McFarland III and correspond to samples in McFarland (1975).

Field samples were crushed with a hammer and 25-50 grams, free of surface weathering and large fossils, were selected for further crushing in a mortar and pestle to about minus 325 mesh. Five grams of the 325 mesh material were treated with 10 ml of concentrated hydrochloric acid for 13-19 hours in a 250 ml Erlenmeyer flask, then diluted with 20 ml of deionized distilled water and filtered through a weighed 0.45 μm Millipore filter. The weight of the undissolved residue was determined and all results were calculated on the amount of material dissolved. The filtrate was diluted to 100 ml with deionized distilled water and analyzed by atomic absorption (A.A) spectrophotometry. Because of the large amount of calcium there was appreciable molecular absorption at the standard A.A. analytical lines and adjacent lines were used to make corrections for this molecular absorption. A summary of the analytical and correction lines is given below.

Element	Analytical Line (A)	Line for Measuring Molecular Absorption (A)
Zn	2139	2100
Cu	3247	2961
Co	2407	2331
Ni	2320	2326

No suitable lines for making corrections for molecular absorption for Pb and Cd could be found and analyses for these elements were abandoned. In the case of nickel where the 2326 A line is not non-absorbing the following relationship was used to find the molecular absorption (m):

$$\frac{B-m}{b-m} = \frac{S}{s} = \text{constant}$$

where B = % absorption of unknown at 2320 A
b = % absorption of unknown at 2326 A
S = % absorption of Ni standard at 2320 A
s = % absorption of Ni standard at 2326 A

Values of B should be kept, by dilution, to 20 and below for greatest accuracy, because the assumption made here is that the absorptions are proportional when in reality it is the absorbances. At low values of B this assumption is approximately true.

Atomic absorption measurements were made with a Perkin Elmer Model 303 spectrophotometer. Recommendations and methods of the Perkin Elmer Handbook (Anonymous, 1973) were followed. Detection limits and sensitivities for the various elements are given in the Handbook. Results in this study are reported to the number of figures considered significant by the author based on noise level and size and reproducability of blanks.

To measure the accuracy of the analytical scheme used here, two standard rock samples were analyzed along with the unknowns. The rock standards, No. 401 and No. 402, are limestone samples from G.

Frederick Smith Company of Columbus, Ohio. Results of our work and that of the supplier are compared in Table 1. Agreement is excellent except in the case of Ba and Fe. In our scheme $BaSO_4$ would not be dissolved. Thus Ba would be low in those samples containing sulfate. In the case of iron there is apparently an appreciable amount in the acid insoluble material which would not be measured in our scheme.

In one set of experiments using St. Joe limestone samples, the relative solvent effects of acetic acid and hydrochloric acid were measured. Acetic acid would not be expected to dissolve, at least in the time intervals employed, iron oxide, pyrite and other expected interstitial compounds. However, because acetic acid does dissolve calcite those atoms substituted for Ca^{++} in the lattice should also be dissolved as well as fluid inclusions. Fluid inclusions have been reported in calcite (p 27 of Wolf, et. al., 1967). These should be dissolved by either of these acids as the calcite is dissolved.

Table 2 compares the relative dissolving power of acetic and hydrochloric acid for 14 elements on 6 samples of St. Joe limestone. Those elements generally showing little or no difference between the two acids are Ca, K, Mn and Sr. Thus it is concluded that these elements are solely in the structure. The elements Na, Ba and Li show an increase of approximately 20% for acetic over hydrochloric acid, which is the same amount that acetic exceeded hydrochloric in acid insoluble material. In other words, calculated on initial weight of sample basis rather than on the basis of "% dissolved", the values for the Na, Ba and Li are the same for the two samples. This indicates that about 20% of these three elements come from easily dissolved structure sources, probably fluid inclusions.

Of the remaining elements, 32% of the magnesium is indicated as coming from non-lattice sources, 45% for Zn, 74% for Fe, 73% for Ni and similarly large amounts for copper and cobalt. Chromium was below detection limit in the case of both acids.

In the above cited experiments with acetic and hydrochloric acids, magnesium was determined by the use of A.A. employing an air-acetylene flame. Calcium results were with a N_2O-acetylene flame and were higher than with air-acetylene for the acetic acid samples. Calcium was the same for both flames on HCl dissolved samples. Apparently there is an acetate complex with calcium which requires the hotter N_2O-acetylene flame to break it. Because of the similarity of Ca and Mg in chemical properties, magnesium was also determined using both flames. The results for calcium and magnesium on acetic acid and HCl dissolved samples using air-acetylene and N_2O-acetylene flames are compared in Table 3. It will be noted that for acetic acid dissolved samples, the results for calcium, on the average, are 29% greater using the N_2O-acetylene flame and only 5% greater for magnesium. Because the higher calcium results agree more closely with the hydrochloric acid values which in turn agreed with the standards, the higher values for calcium are assumed to be the correct ones. The magnesium values are, within experimental error, the same for the two flames.

Discussion

Analyses for Kessler, Brentwood, Pitkin and St. Joe Limestone are summarized respectively in Tables 4, 5, 6 and 7. Locations for the collection dates are also given in the tables. Sample numbers in many cases correspond to those in cited M.S. theses where the lithology, petrography and environment of the samples are given. Average analyses for the four limestones are compared in Table 8.

Important questions are the amount of compositional variation at a given location, from location to location, and for the various limestone formations. The last part of this question is answered in Table 8 by the "per cent of maximum deviation from the average" for the various analyses. These maximum deviations from the average are: 3-5% for Ca and acid insoluble material; 17 to 34% for Co, Li, Cu, Zn, and Ba; 45-56% for Mg, Sr, Na, Ni; 71-108% for Cr, Mn, K, and Fe. These variations are considered small in view of the several million years difference in geologic age and an areal extent of several counties which are represented by the data.

All the limestones are relatively pure $CaCO_3$ with Pitkin having the most acid soluble material, 97.4%, and of this 96.4% was $CaCO_3$ for an overall $CaCO_3$ content of 93.4% (0.974 X 96.4). The remainder is probably moisture (samples were air dried), sulfates, phosphates, aluminates, silicates and organics, materials for which no analyses were made. While having the highest $CaCO_3$ content, the Pitkin was lowest in Mg, Zn, Co, Mn and Li, again indicative of its higher purity. The Kessler limestone was highest in Mg, Cu, Fe, Cr and Mn and lowest in Ca and K. The Brentwood limestone had the lowest average acid soluble material, 90.8%, a relatively high level of Mg, Fe and Mg, but below Kessler and the highest Zn, Li and Sr. St. Joe limestone was about tied with Brentwood for lowest acid soluble material, 90.9%, but had as high a Ca content as Pitkin based on soluble material, 38.6%, the highest K and lowest Fe, Cr, Na and Sr contents, indicative of the high purity of the soluble material.

The last line of Table 8 gives the composition of an average limestone from Wolf, et. al., (1967). The average of the four Northwest Arkansas limestones agree well with this "world" average in the case of Zn, Co, Cr, and Ni and agree with the higher value of 1400 ppm for Mn given by Wolf. Agreement is fair in the cases of Sr (333 ppm vs 475 of reference) and Fe (0.84 wt. % vs 1.13 of reference). Agreement is poorest in the cases of K (44 ppm vs 1600 of reference), Na (156 ppm vs 700 of reference), Cu (2.2 ppm vs 14 of reference), Ba (41 ppm vs 150 of reference) and Li (1.54 ppm vs 20 in reference). We have no explanation for Li but the other differences are believed to be due to the reference using a total analyses, which of course includes acid insoluble material, whereas we have an analysis of only acid soluble material. The much higher Na and K is probably due to the presence of clays in the "world" average samples which were commonly analyzed by emission spectrograph.

Sr/Ca and Mg/Ca average ratios are shown in Table 8 for the four limestones. Kessler and Brentwood are Pennsylvanian age limestones. A Sr/Ca ratio of 0.05 atom % was obtained for these two limestones which compares to 0.072 obtained by Kulp, et. al. (1952) for Indiana limestones of Pennsylvanian age and a range of 0.043-0.13 for various other Pennsylvanian age limestones. The same investigators obtained 0.046 atom % Sr/Ca for Indiana limestones of Mississippian age and a range of 0.014-0.173 for various other Mississippian age limestones. Our two Mississippian age limestones have Sr/Ca atom % ratios of 0.04 (Pitkin) and 0.02 (St. Joe), reasonably close to the Indiana limestone values.

The tabulated analyses for the various limestones in Tables 4 to 7 should be consulted for an appraisal of the vertical variation of the elements from location to location. At a given site the samples differ only in the level of the section from which they were taken. It is difficult to make a general statement for so many locations and for 14 elements.

Three pink limestone samples were selected from St. Joe limestone samples and analyzed in order to determine if their pink color is due to a unique concentration of some element. Manganese was suspected because $MnCO_3$ is pink. However, there is nothing unusual about the Mn concentration nor of other elements. In samples 7 and 8 the pink was concentrated in the acid insoluble material. Because of this the acid insolubles were analyzed and are shown in Table 10. The acid insoluble material are high in Na and K (both colorless ions), and in Fe, Ti and Ni. The latter are probably in ilmenite, a dark mineral. It is suggested that the pink color is due to organic material because the analysis of the inorganic material does not suggest a likely candidate.

The areal variation of Fe, Mg, Mn and Sr for the four limestone formations are shown in Figures 3 to 6. In these figures the North-South distance, using 95° longitude as a base line, and the East-West distance, using 37° latitude as a base line, for a given sampling site have been plotted against the average elemental concentrations for that site. Pitkin limestone shows the least areal variation in the concentration of Fe, Mg and Mn. St. Joe has the least areal variation in Sr concentration. The distances corresponding to the peak concentrations in Figure 3 to 6 have been summarized in Table 9.

Neglecting diagenetic effects and considering only the initial environment of formation, the higher Mg/Ca and Sr/Ca ratio might be expected near shore in lagoons where the life of calcareous secreting organisms fluorished and the ratio of biogenic to inorganic calcite is high. Using this as a criteria, shorelines are indicated for: Kessler Formation at N-S distance of 75 miles and E-W distance of 46 miles; Brentwood Formation at N-S distance of 73 to 79 miles and E-W distance of 36 and 61 miles, Pitkin Formation at N-S distance of 79-80 miles and E-W distance of 39 miles, St. Joe Formation at N-S distances of 36 and 60 miles and E-W distance of 28 and 43 miles. It is interesting that the N-S distance indicative of a shoreline is about the same, 73-80 miles, for the Kessler, Brentwood and Pitkin Formations.

Interrelationships of the metals in limestone are shown in Figures 7-14. In these figures average analyses for a given site are plotted if more than one sample was analyzed from the site. The data are given as atomic % of calcium in many cases. Sr and Na contents of all four limestones correlate well and increase smoothly with Mg content (Figures 7, 8 and 9). In a less precise way, Li, Fe and Zn increase with Mg content. This latter relationship is exemplified by Figure 10 for Mg/Ca versus Zn/Ca. Potassium showed no similar correlation with Mg. Fe and Mn correlate reasonably well, increasing together as shown in Figure 11. Cr tends to increase with Fe while Co and Ni correlate poorly with Fe (Figure 13). Co correlates better with Mn whereas Cr and Ni correlate poorly (Figure 12). Cr correlates better with the sum of the atomic percent of Fe + Mn (Figure 14). Determining the causes of these correlations is very difficult because of many variables and processes involved. Limestone may be formed by inorganic or biogenitic process. Each involves environmental factors. Biogenitic process involve phylogenic factors since different organisms synthesize skeletal material of unique trace element composition.

Implications of these results to the water chemistry of Northwest Arkansas are listed below.

1) Limestones in Northwest Arkansas have normal compositions and are comparable to those of similar geologic ages in other areas. Thus no unusual contributions to the chemistry of the local water is to be expected above the normal contribution to hardness.
2) Of the four limestone formations studied, Kessler has the greatest potential for contributing to the hardness and the heavy metal content of ground water. This is because it has the highest magnesium and heavy metal contents of the various limestones. However, it occurs highest in the stratigraphic column and is least likely to be an aquifer.
3) The following metals in all samples analyzed were at such low concentrations as to pose no problem of water pollution via the route of dissolving limestones: Zn, Cu, Ba and Cr. This statement is based on the following type of calculations. As an upper limit Northwest Arkansas waters contain 50-100 ppm of Ca (Steele et al, 1975). Assuming 100 ppm Ca in the water, that all the calcium comes from a limestone and that the Ca/metal ratios in the limestone persist into the water, then the four limestones would yield water of the following metal contents, using the average analyses for these lime-

stones from Table 8.

ppb

limestone	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr
Kessler	9	1	12	4781	2	3	3	568	0.5	108
Brentwood	11	0.5	<5	3074	2	2	2	401	0.5	113
Pitkin	6	0.6	14	671	1	2	2	84	0.3	88
St. Joe	6	0.5	14	486	2	<0.5	4	448	0.3	44
Limits*	5000	1000	1000	300	-	50	-	50	-	-

Co, Ni. Li and Sr based on the above table would also yield very low concentrations in water from dissolving limestones. However, no safe upper limits.are available for comparison. It will be noted that Fe and Mn could easily exceed their recommended upper limits.

4) It should be emphasized that the above statements are based on averages. A unique composition of any of the limestones might be encountered at a given site. For example, the St. Joe limestone which is the basal member of Boone Formation, a favorite aquifer in Northwest Arkansas, exhibited unusually high Mn and Ni contents at site GCG. Several samples of St. Joe contained pyrite (FeS_2) and could be a source of H_2S in ground water.

---

* U.S. Public Health Service, 1962.

Acknowledgements

We wish to acknowledge the help in sample preparation and in the analyses given by Mr. Robert Tehan and Mr. S. J. Borengasser II. Financial assistance was provided in part by the Office of Water Resources Research Act of 1964, Public Law 88-379 and administered through the Water Resources Research Institute of Arkansas, and the Research Reserve Fund of the University of Arkansas, Fayetteville.

Literature Cited

Anonymous, 1973, Analytical Methods for Atomic Absorption Spectrophotometry, Perkin Elmer Corp., Norwalk, Conn. U.S.A.

Bennett, Robert L., 1965, A petrographic study of a Pitkin reef complex located near Wesley, Arkansas, M.S. Thesis, University of Arkansas.

Graf, D.L., 1960, Geochemistry of carbonate sediments and sedimentary carbonate rocks. Illinois State Geol. Surv. Circ. No. 297, 39 pp.

Hem, John D., 1970, Study and interpretation of the chemical characteristics of natural water: U.S. Geol. Survey Water-Supply Paper 1473, 2nd ed., 363 p.

Kulp, J.L., 1961, Geologic time scale, Science, 133 (No. 3459), 1105-1114.

__________, Turekian, K.K. and Boyd, D.W., 1952, Sr content of limestones and fossils. Bull. Geol. Soc. Am., 63: 701-716.

McFarland, John D. III, 1975, Lithostratigraphy and conodont biostratigraphy of Lower Mississippian strata, Northwest Arkansas, M.S. thesis, University of Arkansas.

Shaji, R. and Folk, R.L., 1964, Surface morphology of some limestone types as revealed by electron microscope. J. Sediment. Petrol., 34: 144-155.

Steele, K.F., MacDonald, H.C. and Grubbs, R.S., 1975, Composition of ground water in Northwest Arkansas, Arkansas Farm Research, January-February, p 15.

U.S. Public Health Service, 1962, Drinking water standards, 1962: U.S. Public Health Service Pub. 956, 61 p.

Wagner, G.H., and Holloway, R.W., 1974, Sodium, potassium, calcium and magnesium content of Northwest Arkansas rain water in 1973 and trace metal analyses of 1974 rains, Arkansas Water Resources Research Center, Publication No. 25.

Wagner, G.H., 1975, Sodium, potassium, calcium and magnesium content of Northwest Arkansas rain water in 1974, Arkansas Water Resources Research Center, Publication No. 29.

Williams, John G., 1975, Sedimentary petrology of the Kessler limestone, Washington and Crawford counties, Arkansas, M.S. thesis, University of Arkansas.

Wolf, K.H., Chilingar, G.V., and Beales, F.W., 1967, Elemental composition of carbonate skeletons, minerals, and sediments, in Developments in Sedimentology 9 B, Carbonate Rocks, Physical and Chemical Aspects (Chilingar, Bissel and Fairbridge editors), Elsevier, New York, N.Y., 413 p.

Table 1

Comparison of Analyses* On Standards
(all data in ppm, except Mg, Ca and Fe in wt.%)

	Standard Sample 401		Standard Sample 402	
Element	This Work	Reference	This work	Reference
Na	100	-	107	-
K	48	-	60	-
Mg	2.35	2.12	3.72	3.40
Ca	36.12	35.91	32.62	33.08
Zn	6	6.9±1.9	5	7.2±1.8
Cu	3	7.2±3.1	1	3.4±1.2
Ba	111	1074	43	26.9
Fe	0.126	0.141	0.095	0.264
Co	2.8	3.0±0.9	1.7	2.2±1.7
Cr	<1	<2	3.5	<2
Ni	7	4.8±2.4	9	7.7±1.1
Mn	99	112 ±9	146	162 ±16
Li	0.96	1.3±0.3	0.89	2.2±0.2
Sr	113	138 ±7	93	103 ±12
% Acid Soluble	97.5	98.0**	95.8	97.5**

* In this work, samples dissolved in concentrated HCl, and insoluble material rejected. In reference, samples dissolved in concentrated HCl, and insoluble material dissolved in sodium metaborate and the two solutions combined for analysis.

** By substraction of % SiO_2 from 100.

Table 2

Comparison of Hydrochloric and Acetic Acids as Solvents for St. Joe Limestones*

(Data in ppm, except Mg, Ca, and Fe in wt. %. All based on amount dissolved)

Sample No.	Acid	% Dissolved	Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr
BV-1	HCl	97.2	81	40	0.202	38.6	15	0.5	47	0.061	4	<1	24	619	1.09	156
BV-1	HOAc	81.8	78	35	0.187	39.2	10	<0.5	38	0.020	2	<1	11	546	1.30	186
BV-2	HCl	84.6	79	241	0.931	38.0	8	8	77	0.274	5	<1	17	669	1.54	202
BV-2	HOAc	73.1	100	211	0.230	39.6	3	<0.5	49	0.045	0.4	<1	1	486	1.31	186
BF-2	HCl	93.5	67	80	0.246	39.1	9	1.0	43	0.068	5	<1	3	425	1.13	216
BF-2	HOAc	68.8	87	74	0.215	39.7	5	<0.5	60	0.016	7	<1	<1	516	1.64	209
BF-3	HCl	96.7	33	52	0.192	39.2	8	1.0	53	0.104	2	<1	5	1051	1.17	124
BF-3	HOAc	75.9	45	67	0.150	39.8	5	<0.5	80	0.036	6	<1	4	1110	1.40	133
WEP-1	HCl	96.5	76	46	0.231	39.6	15	0.5	70	0.121	7	<1	9	781	1.10	158
WEP-1	HOAc	70.0	103	50	0.194	39.8	8	<0.5	44	0.027	2	<1	1	778	1.37	144
WEP-2	HCl	94.6	45	57	0.394	38.4	14	1.5	42	0.128	5	<4	20	1279	1.19	127
WEP-2	HOAc	72.6	58	55	0.162	39.1	8	<0.5	90	0.034	5	<1	4	1192	1.32	128
Average % Difference**		-21	+26	0	-32	+2	-45	-	+19	-74	-	-	-73	-3	+17	+1

* Concentrated HCl, 10 ml on 5 g. limestone for 19 hours.
50% glacial acetic acid (HOAc), 20 ml on 5 g. limestone for 19 hours, then 10 ml 50% glacial acetic for 24 hours.

** 100 (Concentration in HCl - Concentration in HOAc)/(Concentration in HCl)

Table 3

Comparison of N_2O-Acetylene and Air-Acetylene Flames for Analysis of Ca and Mg

		Wt. % of Acid Solubles				Wt. % of Acid Solubles	
	Flame	Calcium		% Deviation(N_2O/air) for:		Magnesium	% Deviation(N_2O/air) for:
Sample No.	Oxidant	HCl*	HOAc*	HCl	HOAc	HOAc*	HOAc
BV-1	air	38.6	29.8			0.187	
	N_2O	38.8	39.2	+ 0.52	+ 31.5	0.197	+ 5.3
BV-2	air	38.0	31.0			0.230	
	N_2O	39.0	39.6	+ 2.6	+ 27.7	0.249	+ 8.3
BV-3	air	37.5	-			-	
	N_2O	36.5	-	- 2.7	-		
BV-4	air	39.7	-			-	
	N_2O	39.9	-	+ 0.50	-		
BV-5	air	36.1	-			-	
	N_2O	37.2	-	+ 3.0	-		
WEP-1	air	39.6	32.0			0.194	
	N_2O	39.8	39.9	+ 0.50	+ 24.7	0.203	+ 4.6
WEP-2	air	38.4	30.2			0.162	
	N_2O	38.5	39.1	+ 0.26	+ 30.1	0.165	+ 1.9
WEP-3	air	39.6	-			-	
	N_2O	38.9	-	- 1.8	-	-	
WEP-4	air	37.4	-			-	
	N_2O	37.3	-	- 0.27	-		
WEP-5	air	40.0	-			-	
	N_2O	39.7	-	- 0.76	-		
BF-1	air	40.0	-			-	
	N_2O	39.8	-	- 0.50	-		
BF-2	air	40.1	31.8			0.215	
	N_2O	39.1	40.1	- 2.5	+ 26.1	0.233	+ 8.4
BF-3	air	39.3	29.5			0.150	
	N_2O	39.2	39.8	- 0.25	+ 34.9	0.155	+ 3.3
BF-4	air	39.3	-			-	
	N_2O	39.4	-	+ 0.25	-		
401**	air	36.1	-			-	
	N_2O	36.5	-	+ 1.1	-		

Table 3 (continued)

		Wt. % of Acid Solubles				Wt. % of Acid Solubles	
	Flame	Calcium		% Deviation(N_2O/air)for:		Magnesium	% Deviation(N_2O/air)for:
Sample No.	Oxidant	HCl*	HOAc*	HCl	HOAc	HOAc*	HOAc
402**	air	32.6	-			-	
	N_2O	34.0	-	+ 4.3	-	-	-
GCG-U3B6	air	37.2	-			-	
	N_2O	38.8	-	+ 4.3	-	-	-
GCG-U3T	air	38.6	-			-	
	N_2O	38.9	-	+ 0.78	-	-	-
GCG-U5A	air	37.7	-			-	
	N_2O	38.2	-	+ 1.3	-	-	-
GCG-U5C	air	38.1	-			-	
	N_2O	39.0	-	+ 2.4	-	-	-
GCG-U6T4	air	37.5	-			-	
	N_2O	43.1	-	+14.9	-	-	-
Average deviation %		-	-	+ 1.3	+ 29.2	-	+ 5.3

* Solvent for limestone, HOAc = acitic acid (50%); HCl = conc. hydrochloric acid.
** Analyses on dry wt. basis, all others on amount dissolved.

Table 4

Kessler Limestone Analyses*
(all data in ppm except Mg, Ca and Fe in wt.%)

Sample	% Acid Soluble	Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr	Location	
																County	Section
Lee Creek, 1-1	91.8	394	22	1.14	35.7	23	2.7	12	1.60	8	6	6	1690	1.21	542	Washington	sec 13,T14N,R31W
Lee Creek, 1-4	95.2	362	14	1.17	34.5	26	2.3	56	4.00	8	17	12	1580	2.02	577	Washington	sec 13, T14N,R31W
Average Lee Creek	93.5	378	18	1.15	35.1	24	2.5	34	2.80	8	11	9	1635	1.61	560		
Devils Den, 3-1	92.2	302	11	0.714	37.1	32	2.2	68	1.76	6	18	16	3480	1.76	488	Washington	E½,sec 23,T13N,R31W
Devils Den, 3-3	89.8	249	26	0.861	36.8	58	3.3	52	2.00	8	14	18	2060	2.61	417	Washington	E½,sec 23,T13N,R31W
Average Devils Den	91.0	275	18	0.787	36.9	45	2.7	60	1.88	7	16	17	2770	2.18	452		
Kessler Mt., 2-3**	93.3	270	12	0.631	36.1	42	2.9	33	1.64	8	13	7	2920	1.74	456	Washington	NE¼,sec 36,T16N,R31W
Kessler Mt., 2-6**	92.7	125	25	0.497	37.3	36	2.9	33	1.42	8	12	9	2400	2.74	221	Washington	NE¼,sec 36,T16N,R31W
Average Kessler Mt.	93.0	197	18	0.564	36.7	39	2.9	33	1.53	8	12	8	2660	2.24	338		
Round Mt., 7-1	95.6	88	17	0.306	37.8	22	2.8	44	0.900	7	7	5	1395	1.05	246	Washington	sec 11,T16N,R29W
Round Mt., 7-3	93.0	134	23	0.375	37.9	37	3.4	57	0.682	5	8	10	1113	1.63	215	Washington	sec 11,T16N,R29W
Average Round Mt.	94.3	111	20	0.340	37.8	29	3.1	50	0.791	6	7	7	1254	1.34	230		
Average of all Kessler Values	92.9	240	19	0.712	36.6	34	2.8	44	1.75	7	12	10	2080	1.84	395		

* All results calculated on basis of amount dissolved
** Type Kessler

Table 5

Brentwood Limestone Analyses*
(all data in ppm, except Mg, Ca and Fe in wt.%)

Sample	% Acid Soluble	Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr	Location County	Location Section
MA1-4	97.0	127	13	0.320	38.1	31	<0.5	<20	0.804	7	5	1	1270	1.53	295	Washington	S½,sec 3,T13N,R33W
MA1-5	79.7	271	112	0.536	37.9	37	3.2	<20	1.39	14	11	14	922	2.95	452	Washington	S½,sec 3,T13N,R33W
Average MA1	88.3	199	63	0.428	38.0	34	1.7	<20	1.10	10	8	8	1096	2.24	373		
CA2-1	93.5	135	29	0.387	38.4	78	0.9	<20	0.896	6	5	10	1116	1.33	390	Crawford	N½,sec 4,T12N,R32W
CA2-4	90.8	267	38	0.549	37.7	47	0.7	<20	1.08	2	5	5	1069	1.63	509	Crawford	N½,sec 4,T12N,R32W
Average CA2	92.1	201	34	0.468	38.0	62	0.8	<20	0.988	4	5	7	1092	1.48	449		
CA4-1	96.0	115	19	0.335	38.6	29	<0.5	<20	0.460	7	5	4	990	1.44	323	Washington	SW¼,sec 1,T13N,R32W
CA4-4	98.1	91	15	0.297	38.9	32	<0.5	<20	0.585	8	5	<1	1305	1.41	316	Washington	SW¼,sec 1,T13N,R32W
Average CA4	97.0	103	17	0.316	38.7	30	<0.5	<20	0.522	8	5	2	1147	1.42	319		
HS3-1**	33.4	206	78	0.428	39.3	43	1.3	<20	2.33	5	17	13	1329	0.94	1057	Washington	N½,sec 4,T13N,R32W
HS4-3	95.6	153	36	0.416	38.8	13	0.5	49	1.24	4	4	<1	1231	1.77	362	Washington	N½,sec 22,T14N,R32W
HS4-4	91.5	305	49	0.621	38.1	19	0.7	<20	1.78	4	10	6	1340	2.36	409	Washington	N½,sec 22,T14N,R32W
Average HS4	93.5	229	42	0.518	38.4	16	0.6	25	1.51	4	7	3	1285	2.06	385		
MA2-3	94.3	115	38	0.301	39.4	24	<0.5	<20	0.578	5	5	10	2139	1.54	245	Washington	NW¼,sec 10,T14N,R32W
MA2-5	96.2	119	18	0.543	37.6	25	<0.5	<20	1.29	9	6	3	1577	1.31	322	Washington	NW¼,sec 10,T14N,R32W
Average MA2	95.2	117	28	0.422	38.5	24	<0.5	<20	0.934	7	6	7	1858	1.42	283		
CE-1	95.3	241	12	0.534	37.0	37	1.3	<20	0.577	4	7	1	1315	1.88	325	Madison	SW¼,sec 11,T14N,R28W
CE-2	57.3	489	162	1.10	36.5	105	9.0	<20	2.07	10	15	28	1649	5.58	719	Madison	SW¼,sec 11,T14N,R28W
Average CE	76.3	365	87	0.817	36.7	71	5.1	<20	1.32	7	11	14	1482	3.73	522		
T-1	94.8	127	22	0.436	36.6	22	2.5	<20	0.869	6	6	1	2189	1.22	435	Madison	SE¼,sec 34,T15N,R28W
T-2	93.8	287	31	1.71	32.7	55	2.5	39	4.21	13	15	1	4184	1.71	585	Madison	SE¼,sec 34,T15N,R28W
Average T	94.3	207	26	1.07	34.6	38	2.5	20	2.54	9	10	6	3186	1.46	510		
LB-1	87.9	372	75	0.867	39.0	69	3.2	<20	1.04	10	7	3	2177	2.54	625	Madison	NE¼,sec 33,T15N,R27W
K-4	93.4	130	25	0.561	39.1	19	1.4	32	0.532	4	5	<1	699	1.24	513	Madison	SE¼,sec 2,T15N,R26W
K-8(L)	88.1	210	33	0.481	39.1	35	1.4	23	0.404	3	6	<1	689	1.43	476	Madison	SE¼,sec 2,T15N,R26W
Average K	90.7	170	29	0.521	39.1	27	1.4	27	0.468	4	5	<1	694	1.33	494		
Average Brentwood	90.8	209	43	0.588	37.9	40	1.7	20	1.165	7	7	6	1521	1.93	429		

* all results calculated on basis of amount dissolved

** by definition not a limestone due to <50% acid solubility.

Table 6

Pitkin Limestone Analyses*

(all data in ppm, except Mg, Ca and Fe in wt.%)

Sample	% Acid Soluble	Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr	Location	
																County	Section
Mt. Fork Cr. MF-1	96.4	84	32	0.249	39.7	22	2.4	<11	0.477	7	8	1	912	1.24	275	Crawford	SW¼,sec 24,T12N,R33W
Mt. Fork Cr. MF-2	97.8	76	33	0.305	38.6	14	2.2	28	0.341	6	7	<1	358	1.03	383	Crawford	SW¼,sec 24,T12N,R33W
Mt. Fork Cr. MF-3	99.1	49	7	0.242	38.8	4	1.3	11	0.256	4	7	4	338	0.82	328	Crawford	SW¼,sec 24,T12N,R33W
Average Mt. Fork	97.8	70	24	0.265	39.0	13	2.0	15	0.358	6	7	2	536	1.03	329		
Quarry, Q1-P	94.4	120	22	0.379	38.6	23	4.2	67	0.203	5	13	9	239	1.50	503	Wash.	SE¼,sec 1,T13N,R32W
Quarry, Q2-P	94.1	145	26	0.442	38.6	21	7.0	29	0.185	1	11	9	239	1.40	531	Wash.	SE¼,sec 1,T13N,R32W
Quarry, Q3-P	98.4	77	9	0.266	37.7	18	2.0	<11	0.177	2	11	3	856	1.13	330	Wash.	SE¼,sec 1,T13N,R32W
Quarry, Q4-P	97.4	109	8	0.374	38.3	14	2.4	32	0.270	1	12	3	292	1.36	437	Wash.	SE¼,sec 1,T13N,R32W
Average Quarry	96.1	113	16	0.365	38.3	19	3.9	33	0.209	2	12	6	406	1.35	450		
Cove Cr. Rd, CCR-1	98.6	47	9	0.258	38.8	14	2.3	43	0.266	6	8	6	162	1.22	347	Wash.	N½,sec 1,T13N,R32W
Cove Cr. Rd, CCR-2	97.7	65	14	0.305	39.2	26	3.3	59	0.205	4	9	7	179	1.35	353	Wash.	N½,sec 1,T13N,R32W
Cove Cr. Rd, CCR-3	97.7	53	8	0.298	39.2	29	3.3	<11	0.250	5	8	5	307	1.03	333	Wash.	N½,sec 1,T13N,R32W
Average Cove Cr. Rd	98.0	55	10	0.287	39.1	23	3.0	36	0.240	5	8	6	216	1.20	344		
Lithographic, A3**	98.8	81	17	0.352	38.4	5	0.4	<110	0.194	1	6	1	169	1.11	357	Madison	NW½,NW¼,sec 17,T15N,R27W
Lithographic, E-2	96.8	337	59	0.477	38.2	59	2.7	162	0.624	1	13	22	137	1.21	644	Madison	NW½,NW¼,sec 17,T15N,R27W
Av. Lithographic	97.8	209	38	0.414	38.3	32	1.5	109	0.409	1	9	11	153	1.16	500		
Algal Reef, 1-4	96.1	70	38	0.252	37.5	24	1.2	163	0.191	9	10	6	287	1.33	234	Madison	NW½,NW¼,sec 17,T15N,R27W
Algal Reef, 1-6	97.3	59	22	0.180	38.5	35	1.3	<110	0.208	5	11	6	321	1.20	214	Madison	NW½,NW¼,sec 17,T15N,R27W
Average Algal Reef	96.7	64	30	0.216	38.0	29	1.3	109	0.199	7	10	6	304	1.26	224		
Crinoidal, W-7	98.6	63	17	0.154	38.6	25	0.9	<110	0.162	<3	8	4	206	1.01	195	Madison	NW½,NW¼,sec 17,T15N,R27W
Crinoidal, C-8	98.8	86	35	0.173	37.8	16	0.6	111	0.122	18	6	5	242	1.01	195	Madison	NW½,NW¼,sec 17,T15N,R27W
Av. Crinoidal	98.7	74	26	0.164	38.2	20	0.7	83	0.142	10	7	4	223	1.01	195		
Oolitic 1-8	99.0	55	25	0.202	38.2	30	1.6	<110	0.310	<6	8	4	352	1.14	194	Madison	NW½,NW¼,sec 17,T15N,R27W
Bryazoan, AA-5	96.1	98	36	0.202	39.3	25	0.9	<110	0.230	9	8	6	258	1.22	238	Madison	NW½,NW¼,sec 17,T15N,R27W
Average Bennett	97.7	106	31	0.249	38.3	27	1.2	89	0.255	6	9	7	246	1.15	284		
Average Pitkin	97.4	93	23	0.284	38.6	22	2.2	55	0.259	5	9	6	325	1.18	338		

* all results calculated on basis of amount dissolved

** This and following numbers correspond to sample numbers in Bennett, 1965.

Table 7

St. Joe Limestone Analyses*
(all data in ppm, except Mg, Ca and Fe in wt.%)

Sample**	% Acid Soluble	Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr	Location	
																County	Section
BV-1 (5)	97.2	81	40	0.202	38.6	15	0.5	47	0.061	4	1	24	619	1.09	156	Benton	NW¼,NW¼,sec 23,T21N,R31W
BV-2 (3)	84.6	79	241	0.931	38.0	8	8.0	77	0.274	5	1	17	669	1.54	202	Benton	NW¼,NW¼,sec 23,T21N,R31W
BV-3 (-)	78.4	96	252	1.278	36.5	12	2.0	46	0.522	12	4	10	811	2.22	196	Benton	NW¼,NW¼,sec 23,T21N,R31W
BV-4 (2)	86.5	67	173	0.385	39.4	173	2.0	75	0.183	8	1	12	388	1.50	176	Benton	NW¼,NW¼,sec 23,T21N,R31W
BV-5 (4)	83.9	126	192	1.90	36.1	8	4.0	77	0.594	9	3	14	865	1.83	204	Benton	NW¼,NW¼,sec 23,T21N,R31W
Average BV	86.1	90	180	0.940	37.7	43	3	64	0.327	8	2	15	670	1.64	187		
WEP-1 (4)	96.5	76	46	0.231	39.6	15	0.5	70	0.121	7	1	9	781	1.10	158	Benton	SW¼,NE¼,sec 24,T18N,R29W
WEP-2 (5)	94.6	45	57	0.394	38.4	14	1.5	42	0.128	5	1	20	1270	1.19	127	Benton	SW¼,NE¼,sec 24,T18N,R29W
WEP-3 (6)	94.6	49	60	0.449	38.9	121	3.0	26	0.182	7	1	16	955	1.01	127	Benton	SW¼,NE¼,sec 24,T18N,R29W
WEP-4 (2)	93.5	91	100	1.00	37.4	7	2.5	70	0.809	9	1	17	599	1.39	183	Benton	SW¼,NE¼,sec 24,T18N,R29W
WEP-5 (3)	94.8	50	62	0.185	39.7	11	0.5	38	0.150	3	1	3	605	1.12	127	Benton	SW¼,NE¼,sec 24,T18N,R29W
Average WEP	94.8	62	65	0.452	38.8	34	1.6	49	0.278	6	1	13	844	1.16	144		
BF-1 (3)	98.8	43	16	0.181	39.8	10	3.0	44	0.525	1	1	7	675	0.97	138	Madison	N½,NW¼,sec 1,T17N,R27W
BF-2 (1)	93.5	67	80	0.246	39.1	9	1.0	43	0.068	5	1	3	425	1.13	216	Madison	N½,NW¼,sec 1,T17N,R27W
BF-3 (4)	96.7	33	52	0.192	39.2	8	1.0	53	0.104	2	1	5	1051	1.17	124	Madison	N½,NW¼,sec 1,T17N,R27W
BF-4 (2)	97.9	26	28	0.192	39.4	8	2.0	41	0.081	1	1	4	749	1.40	123	Madison	N½,NW¼,sec 1,T17N,R27W
Average BF	96.7	42	44	0.203	39.3	9	1.8	35	0.194	2	1	5	725	1.17	150		
GCG-U3B6(2)	65.4	72	120	0.581	38.8	26	1.0	70	0.086	9	3	2	2635	1.10	173	Benton	SW¼,NW¼,sec 32,T17N,R33W
GCG-U3T (3)	82.5	114	100	0.478	38.9	13	5.0	62	0.077	11	3	11	3287	1.48	188	Benton	SW¼,NW¼,sec 32,T17N,R33W
GCG-U5A (5)	79.9	140	61	0.577	38.2	17	3.0	81	0.269	7	4	17	3985	0.90	229	Benton	SW¼,NW¼,sec 32,T17N,R33W
GCG-U5C (8)	97.1	80	13	0.201	39.0	11	0.5	32	0.023	9	3	6	4185	0.92	160	Benton	SW¼,NW¼,sec 32,T17N,R33W
GCG-U6T4 (12)	93.5	158	43	0.245	39.7	18	6.0	48	0.120	24	3	101	10621	1.03	253	Benton	SW¼,NW¼,sec 32,T17N,R33W
Average GCG	83.7	113	67	0.416	38.9	17	3.1	59	0.115	12	3	27	4943	1.08	201		
Pink 6	97.8	101	97	0.172	39.8	2	1	27	0.042	3	-	9	1461	1.11	161	Carroll	SE¼,NW½,sec 15,T18N,R23W
Pink 7	95.8	81	115	0.164	39.8	10	1	27	0.123	1	-	3	714	1.04	164	Carroll	NW¼,sec 10,T20N,R27W
Pink 8	97.1	104	61	0.165	39.8	10	1	69	0.058	1	-	4	806	0.86	162	Searcy	NE¼,sec 18,T16N,R17W
Average, all St. Joe	90.9	81	91	0.470	38.7	24	2	53	0.188	7	2	14	1735	1.23	170		

*all results calculated on basis of amount dissolved.

**numbers in parentheses correspond to numbers in McFarland, 1975

Table 8

Summary

Average Aanlyses for Kessler, Brentwood, Pitkin and St. Joe Limestones

Limestone	Geologic Age(10^6yr)*	% Acid Soluble	ppm (except Mg, Ca, Fe in wt.%)														atom %	
			Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Cr	Ni	Mn	Li	Sr	Sr/Ca	Mg/Ca
Kessler	280–310	92.9	240	19	0.712	36.6	34	2.8	44	1.75	7	12	10	2080	1.84	395	0.05	3.1
Brentwood	280–310	90.8	209	43	0.588	37.9	40	1.7	<20	1.165	7	7	6	1521	1.93	429	0.05	2.6
Pitkin	310	97.4	93	23	0.284	38.6	22	2.2	55	0.259	5	9	6	325	1.18	338	0.04	1.2
St. Joe	340	90.9	81	91	0.470	38.7	24	2.0	53	0.188	7	<2	14	1735	1.23	170	0.02	2.0
Average of above		93.0	156	44	0.513	37.9	30	2.2	41	0.840	6	7	9	1415	1.54	333	0.04	2.2
Max. % Deviation from average		4.7%	54%	107%	45%	3.4%	33%	27%	34%	108%	17%	71%	56%	77%	25%	49%	50%	45%
"World" average** is		-	700	1600	-	-	26	14	150	1.13	4.3	9	12	500–1400	20	475	-	-

* Ages of Mississippian and Pennsylvanian taken from Kulp (1961). Pitkin is known to be of earliest Mississippian and St. Joe of latest Mississippian age. Kessler is youngest and Brentwood oldest of Bloyd Formation which is Late Pennsylvanian.

** Limestone average taken from Table III, page 50, of Wulf, et. al. (1967) which represents an average of many published analyses.

Table 9

Peaks in Areal Distribution of Fe, Mg, Mn and Sr for Various Limestones Summarized from Figures 3-6

Limestone	Element	North-South (Miles*)			East-West (Miles*)	
		major	minor	minor	major	minor
Kessler	Mg	75	-	-	46	-
	Mn	82	65	-	46	-
	Sr	75	-	-	46	-
	Fe	44	-	-	82	-
Brentwood	Mg	73	-	-	61	37
	Mn	73	-	-	61	37
	Sr	79	74	85	36	66
	Fe	61	36	-	73	79
Pitkin	Mg	79	-	-	39	-
	Mn	88	-	-	30	-
	Sr	80	-	-	39	-
	Fe	31	-	-	88	-
St. Joe	Mg	36	53	60	43	-
	Mn	61	-	-	93	59
	Sr	60	35	-	28	-
	Fe	43	-	-	36	53

* Distances are measured from 37° latitude for North-South, and from 95° longitude for East-West.

Table 10

Analyses of Pink St. Joe Limestone

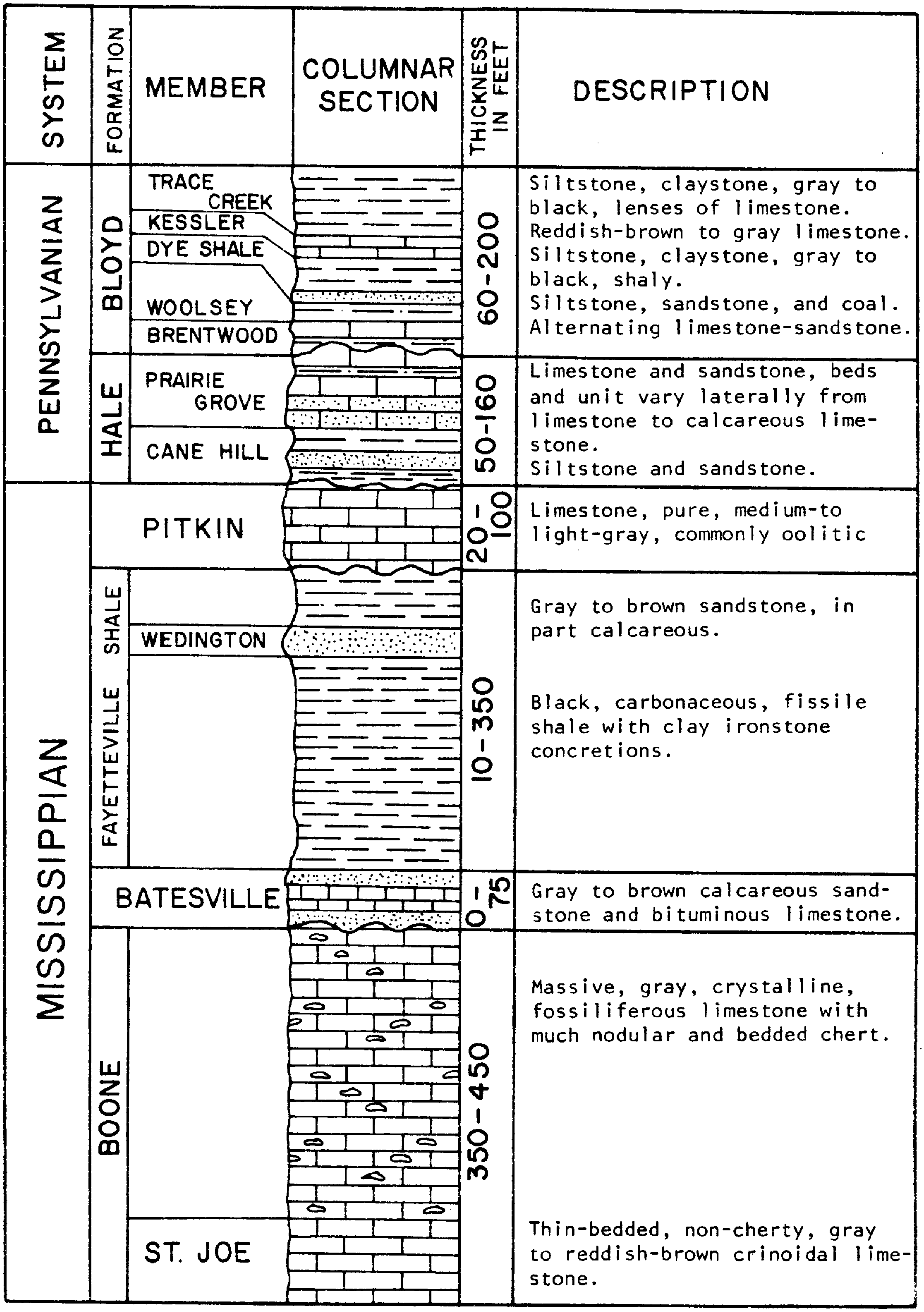
ppm (except Mg, Ca and Fe in wt. %)

Sample*	Na	K	Mg	Ca	Zn	Cu	Ba	Fe	Co	Ni	Mn	Li	Sr	V	Ti	Ta
7 - acid solubles	78	114	0.157	38.59	12	<1	26	0.1180	<1	3	684	1.00	157	12	31	<86
7 - sol. + insol.	159	1709	0.226	38.59	16	13	35	0.2079	<1	12	689	2.42	158	<8	275	<82
7 - acid insol.	1952	38434	1.67	<0.02	96	313	217	2.17	<24	217	120	34	24	12	5880	<1976
8 - acid solubles	101	63	0.161	39.63	12	<1	67	0.0565	<1	4	783	0.86	157	12	37	<86
8 - sol. + insol.	115	1206	0.199	39.63	15	4	73	0.1406	3	19	800	1.53	159	<8	226	<82
8 - acid insol.	49	40105	1.36	<0.028	105	140	211	2.95	105	526	596	24	70	12	6632	<1976
6 - acid solubles	99	95	0.168	38.92	2	<1	26	0.0414	3	9	1458	1.09	157	8	20	<84

* acid solubles, based on what dissolved in concentrated HCl and calculated on total sample weight.
acid solubles + insolubles, based on what dissolved in concentrated HCl + HF and calculated on total sample weight.
acid insolubles, based on HF solubles of HCl insolubles and calculated on weight of HCl insolubles.

Figure 1

A Generalized Stratigraphic Column for Northwest Arkansas



SYSTEM	FORMATION	MEMBER	THICKNESS IN FEET	DESCRIPTION
PENNSYLVANIAN	BLOYD	TRACE CREEK	60-200	Siltstone, claystone, gray to black, lenses of limestone.
		KESSLER		Reddish-brown to gray limestone.
		DYE SHALE		Siltstone, claystone, gray to black, shaly.
		WOOLSEY		Siltstone, sandstone, and coal.
		BRENTWOOD		Alternating limestone-sandstone.
	HALE	PRAIRIE GROVE	50-160	Limestone and sandstone, beds and unit vary laterally from limestone to calcareous limestone.
		CANE HILL		Siltstone and sandstone.
MISSISSIPPIAN	PITKIN		20-100	Limestone, pure, medium-to light-gray, commonly oolitic
	FAYETTEVILLE SHALE		10-350	
		WEDINGTON		Gray to brown sandstone, in part calcareous.
				Black, carbonaceous, fissile shale with clay ironstone concretions.
	BATESVILLE		0-75	Gray to brown calcareous sandstone and bituminous limestone.
	BOONE		350-450	Massive, gray, crystalline, fossiliferous limestone with much nodular and bedded chert.
		ST. JOE		Thin-bedded, non-cherty, gray to reddish-brown crinoidal limestone.

Figure 2

Sampling Locations

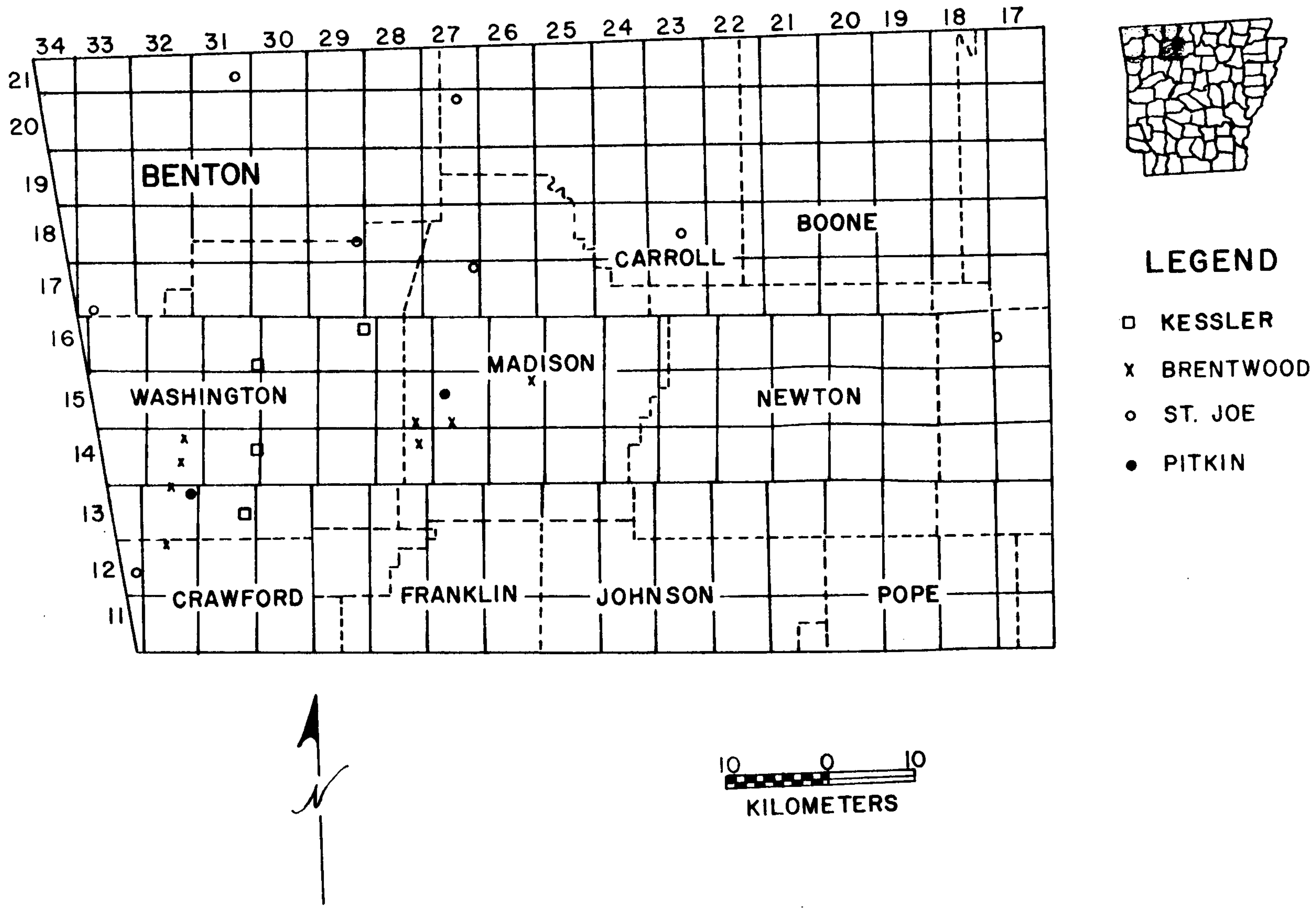
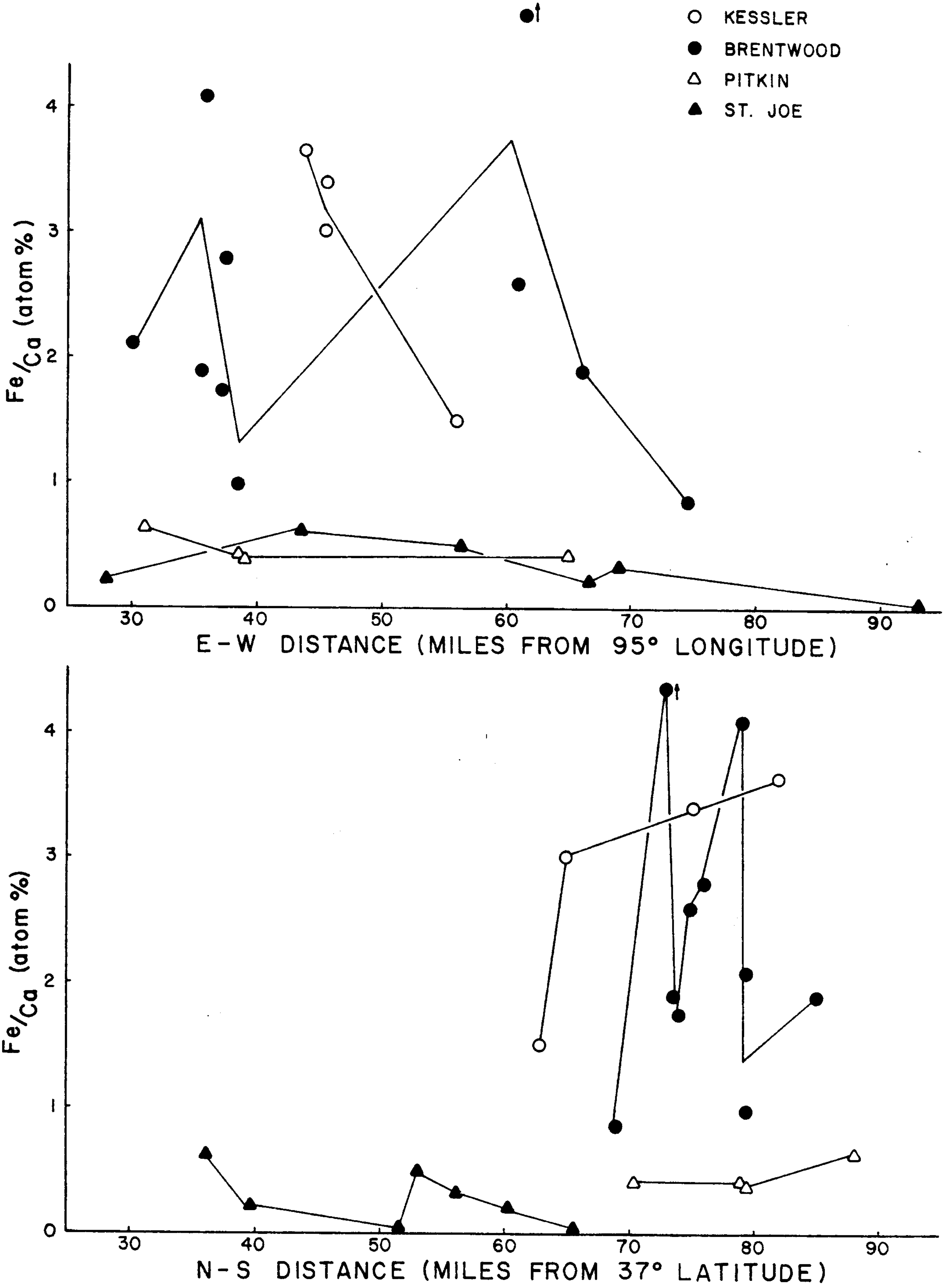

34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
21
20
19
18
17
16
15
14
13
12
11
BENTON
CARROLL
BOONE
MADISON
WASHINGTON
NEWTON
CRAWFORD
FRANKLIN
JOHNSON
POPE
LEGEND
□ KESSLER
x BRENTWOOD
○ ST. JOE
● PITKIN
N
10
0
10
KILOMETERS

Figure 3

E-W and N-S Variation of Fe Content of Limestones



○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Fe/Ca (atom %)
0
1
2
3
4
30
40
50
60
70
80
90
E-W DISTANCE (MILES FROM 95° LONGITUDE)
Fe/Ca (atom %)
0
1
2
3
4
30
40
50
60
70
80
90
N-S DISTANCE (MILES FROM 37° LATITUDE)

Figure 4

E-W and N-S Variation of Mg Content of Limestones

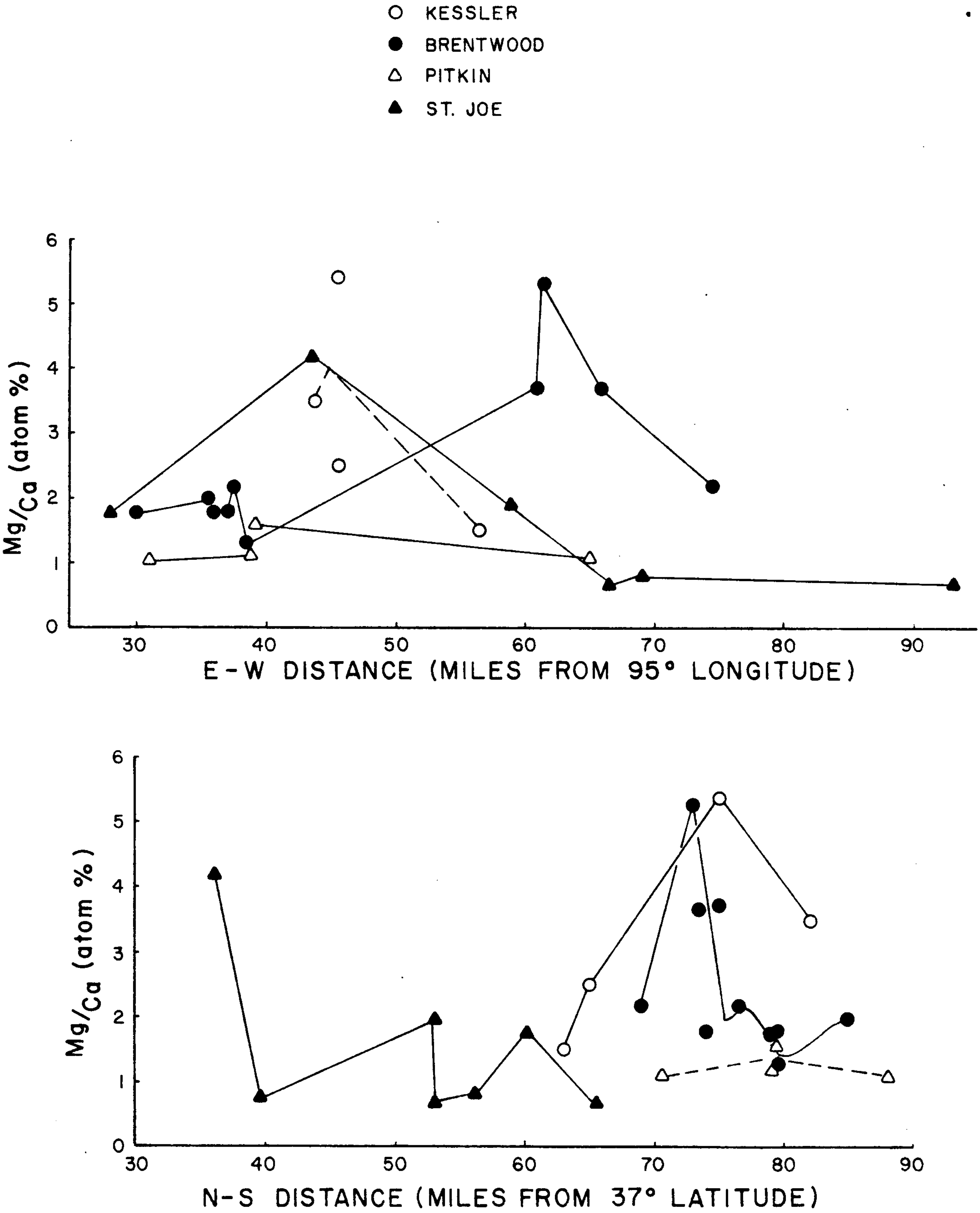
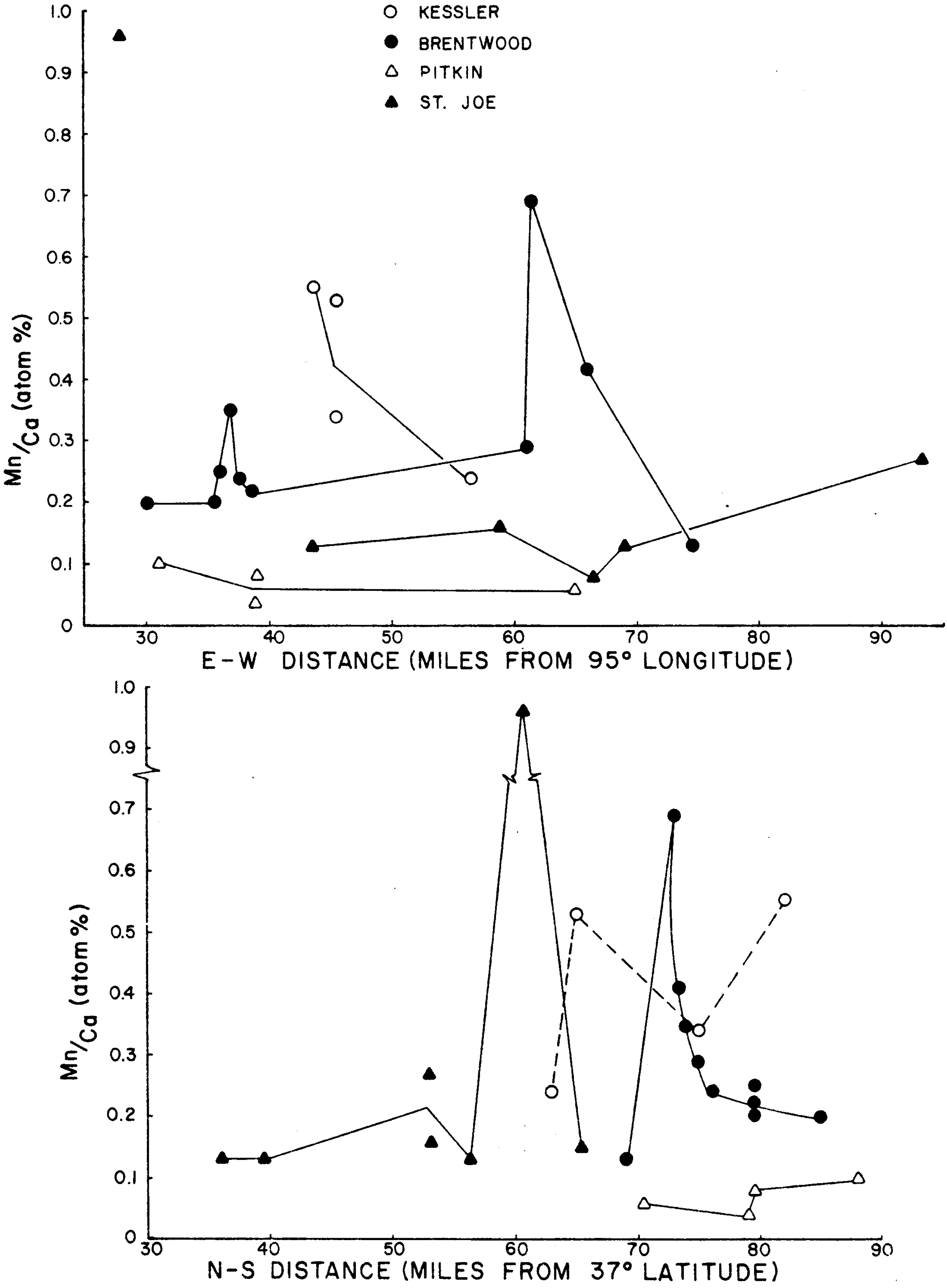

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Mg/Ca (atom %)
0
1
2
3
4
5
6
30
40
50
60
70
80
90
E-W DISTANCE (MILES FROM 95° LONGITUDE)
Mg/Ca (atom %)
0
1
2
3
4
5
6
30
40
50
60
70
80
90
N-S DISTANCE (MILES FROM 37° LATITUDE)

Figure 5

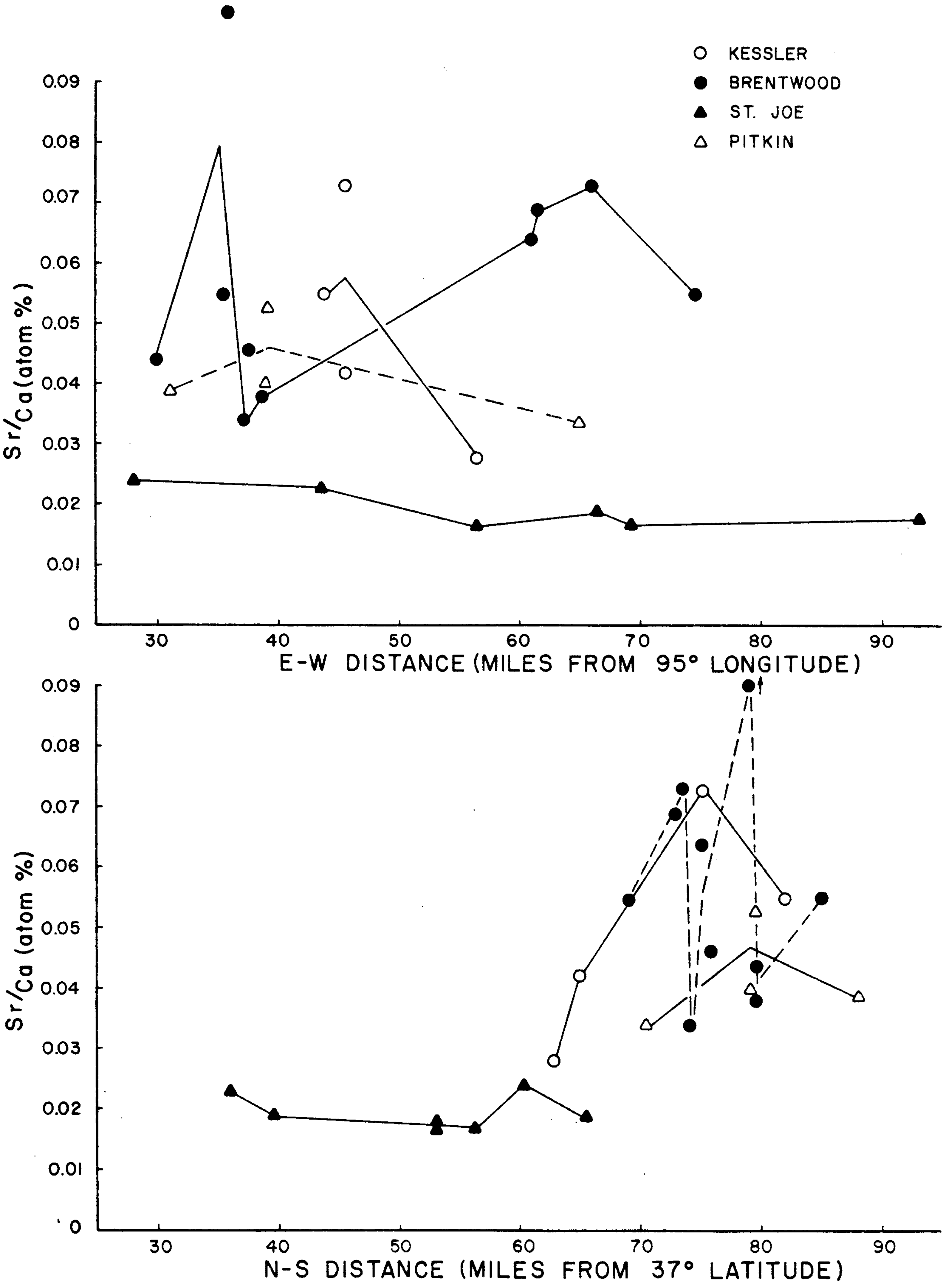
E-W and N-S Variation of Mn Content of Limestones



○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Mn/Ca (atom %)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
30
40
50
60
70
80
90
E-W DISTANCE (MILES FROM 95° LONGITUDE)
Mn/Ca (atom %)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.9
1.0
30
40
50
60
70
80
90
N-S DISTANCE (MILES FROM 37° LATITUDE)

Figure 6

E-W and N-S Variation of Sr Content of Limestones



○ KESSLER
● BRENTWOOD
▲ ST. JOE
△ PITKIN
Sr/Ca (atom %)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
30
40
50
60
70
80
90
E-W DISTANCE (MILES FROM 95° LONGITUDE)
Sr/Ca (atom %)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
30
40
50
60
70
80
90
N-S DISTANCE (MILES FROM 37° LATITUDE)

Figure 7

Na/Ca Ratio versus Mg/Ca Ratio of Limestones

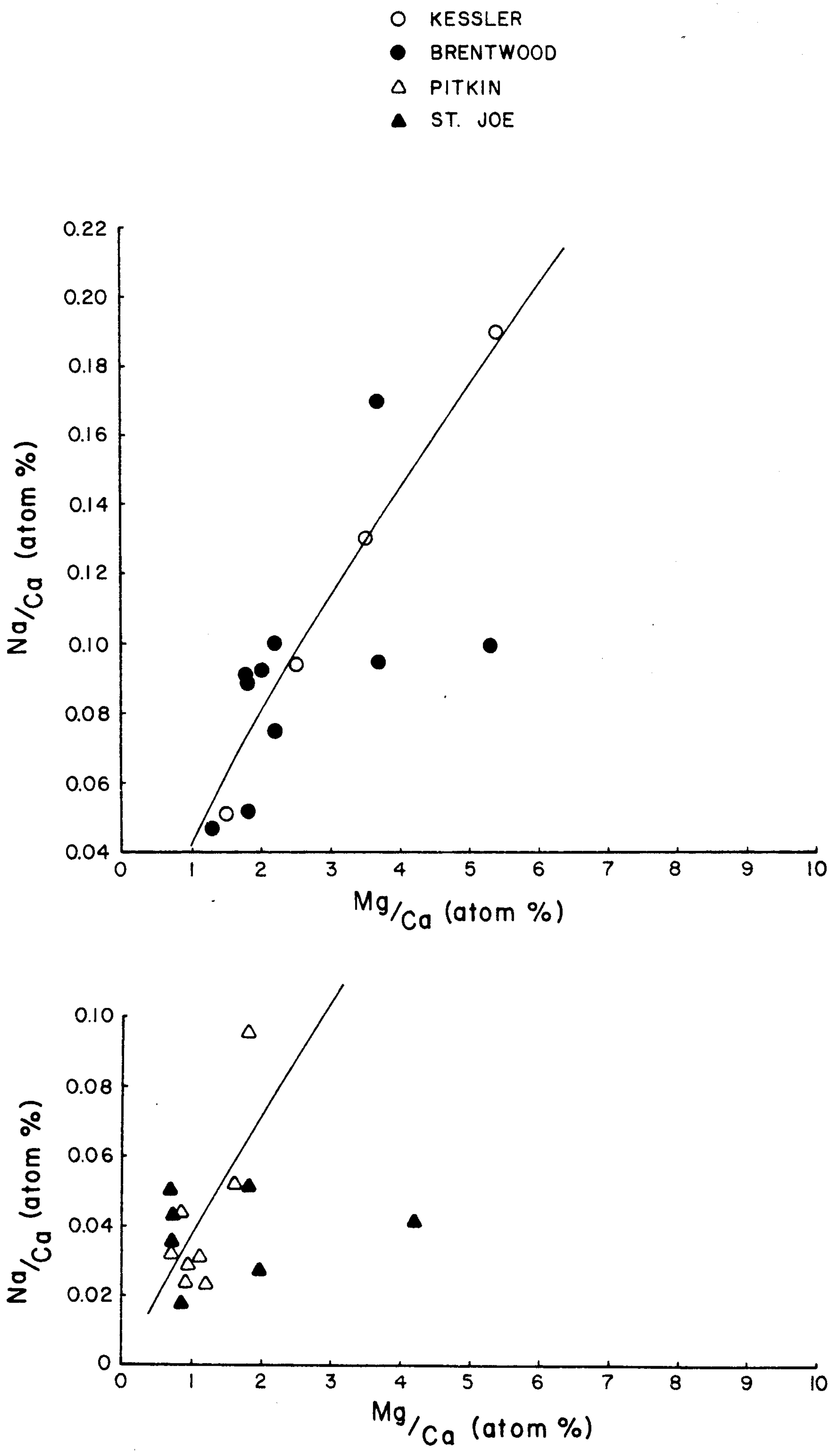

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
Na/Ca (atom %)
0 1 2 3 4 5 6 7 8 9 10
Mg/Ca (atom %)
0.10
0.08
0.06
0.04
0.02
0
Na/Ca (atom %)
0 1 2 3 4 5 6 7 8 9 10
Mg/Ca (atom %)

Figure 8

Sr/Ca Ratio versus Mg/Ca Ratio of Limestones

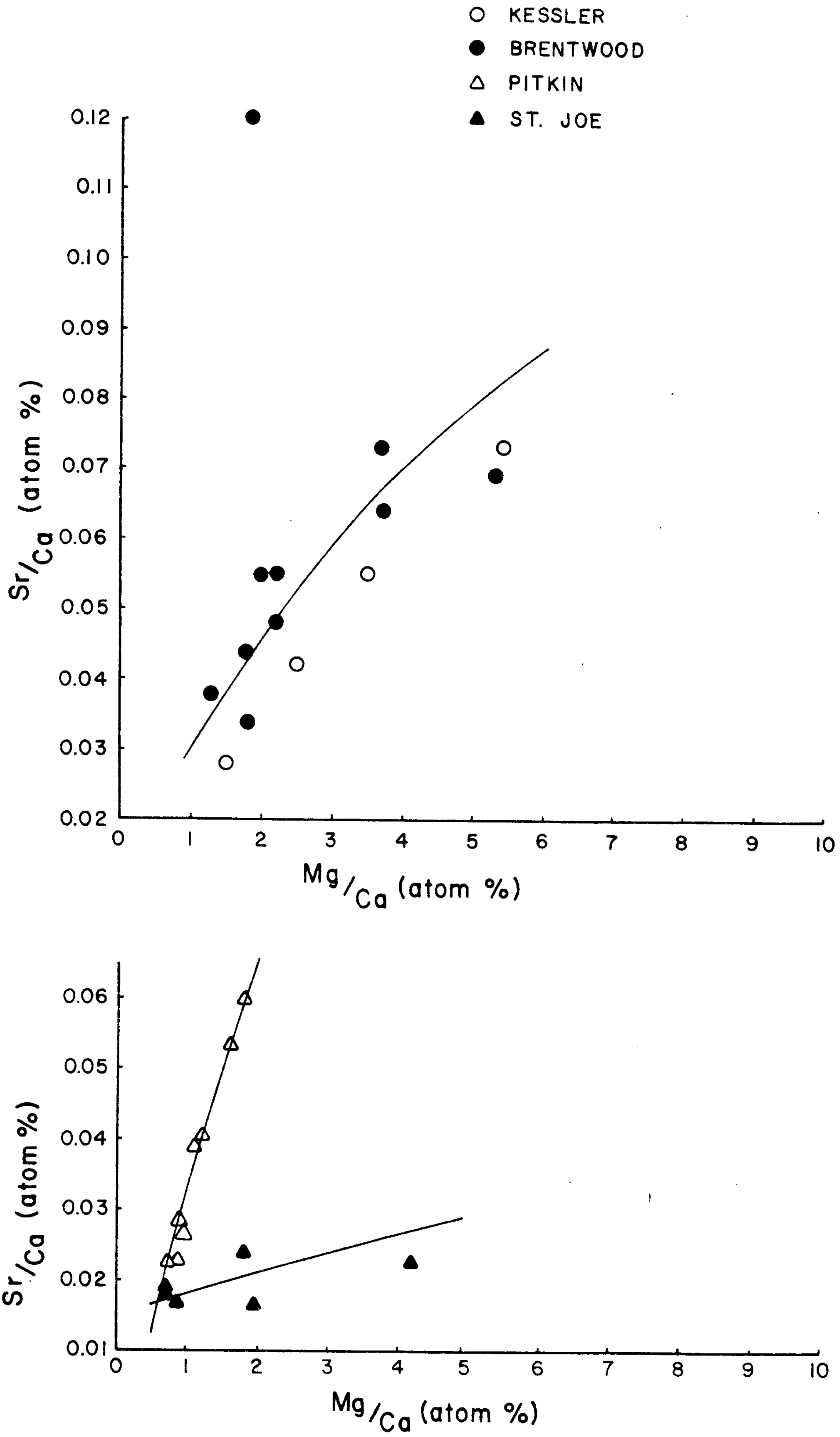

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
Sr/Ca (atom %)
0
1
2
3
4
5
6
7
8
9
10
Mg/Ca (atom %)
0.06
0.05
0.04
0.03
0.02
0.01
Sr/Ca (atom %)
0
1
2
3
4
5
6
7
8
9
10
Mg/Ca (atom %)

Figure 9

Sr/Ca Ratio versus Na/Ca Ratio of Limestones

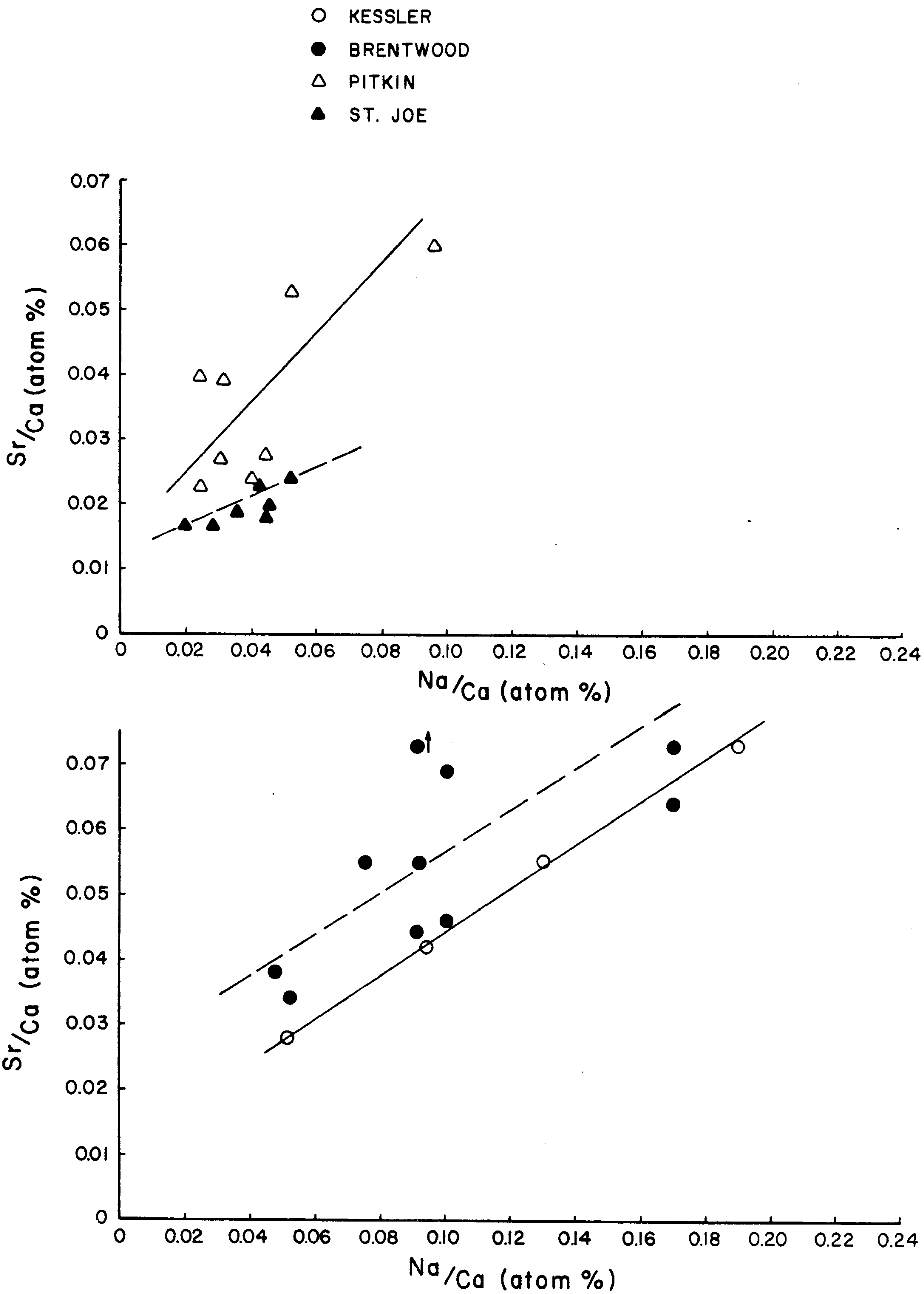

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Sr/Ca (atom %)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
Na/Ca (atom %)
Sr/Ca (atom %)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
Na/Ca (atom %)

Figure 10

Zn/Ca Ratio versus Mg/Ca Ratio of Limestones

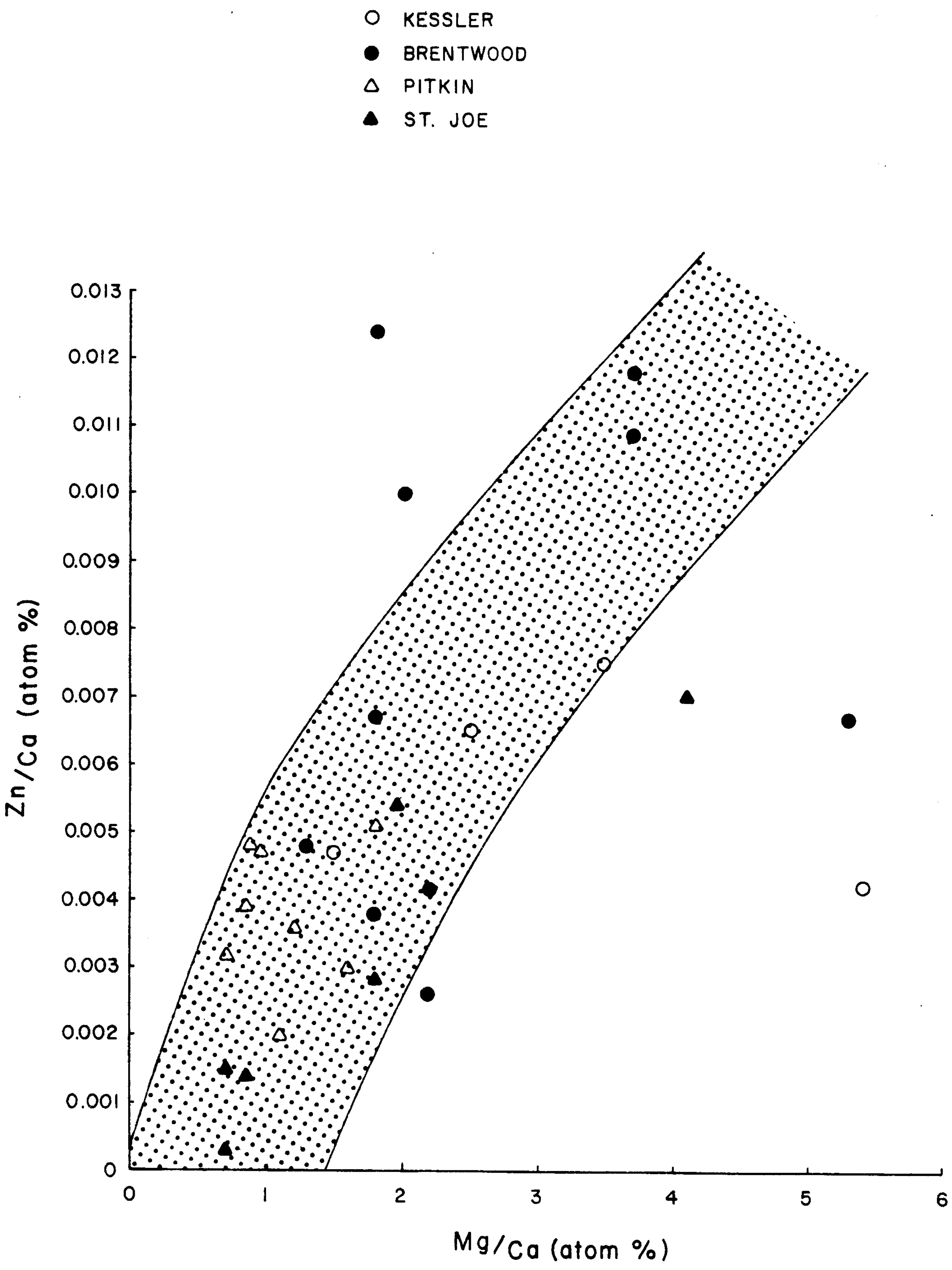

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Zn/Ca (atom %)
0
1
2
3
4
5
6
Mg/Ca (atom %)

Figure 11

Mn/Ca Ratio versus Fe/Ca Ratio of Limestones

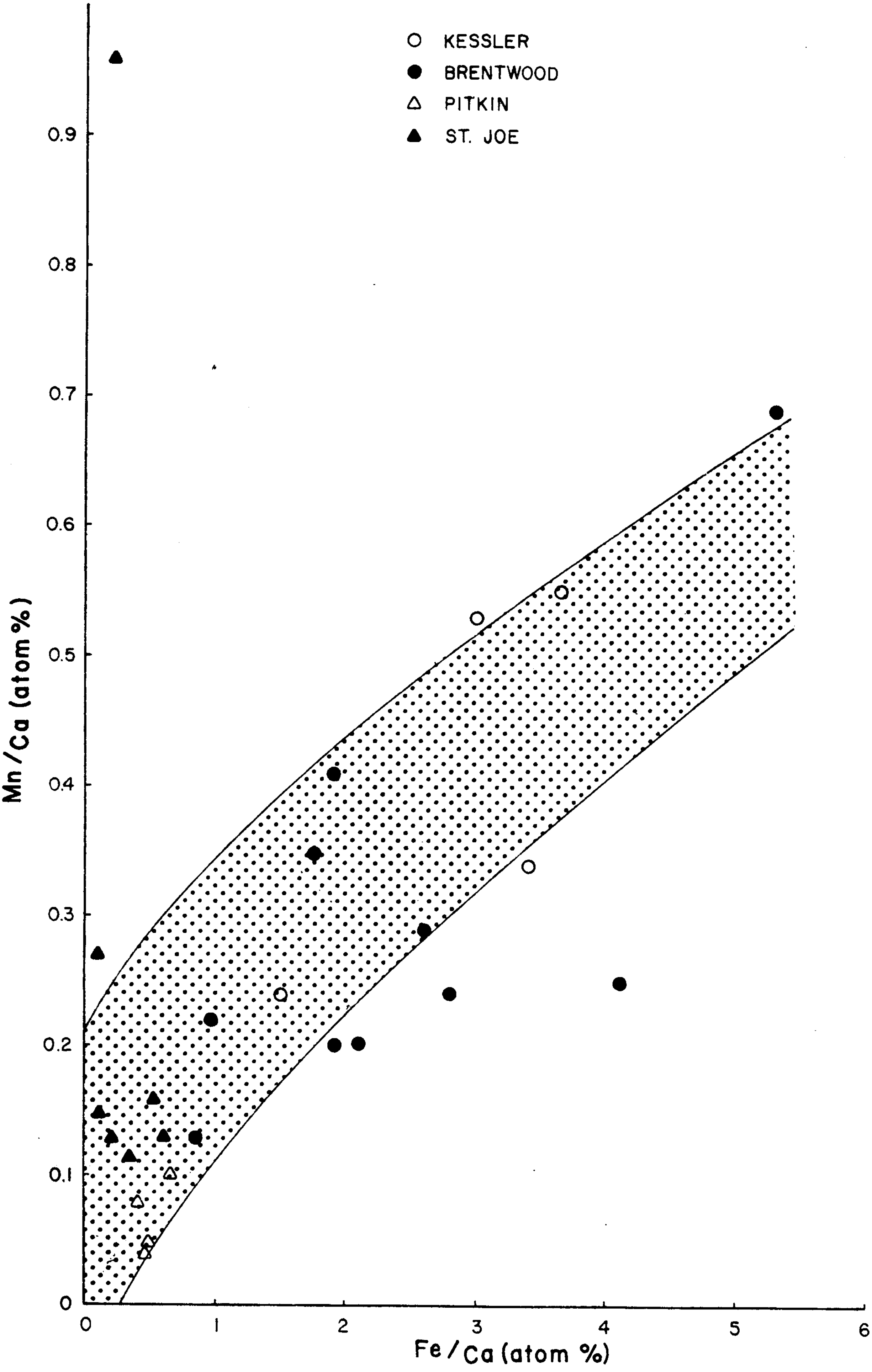

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Mn / Ca (atom %)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Fe / Ca (atom %)
0
1
2
3
4
5
6

Figure 12

Co, Cr and Ni Content versus Mn Content for Kessler, Brentwood, Pitkin and St. Joe Limestones

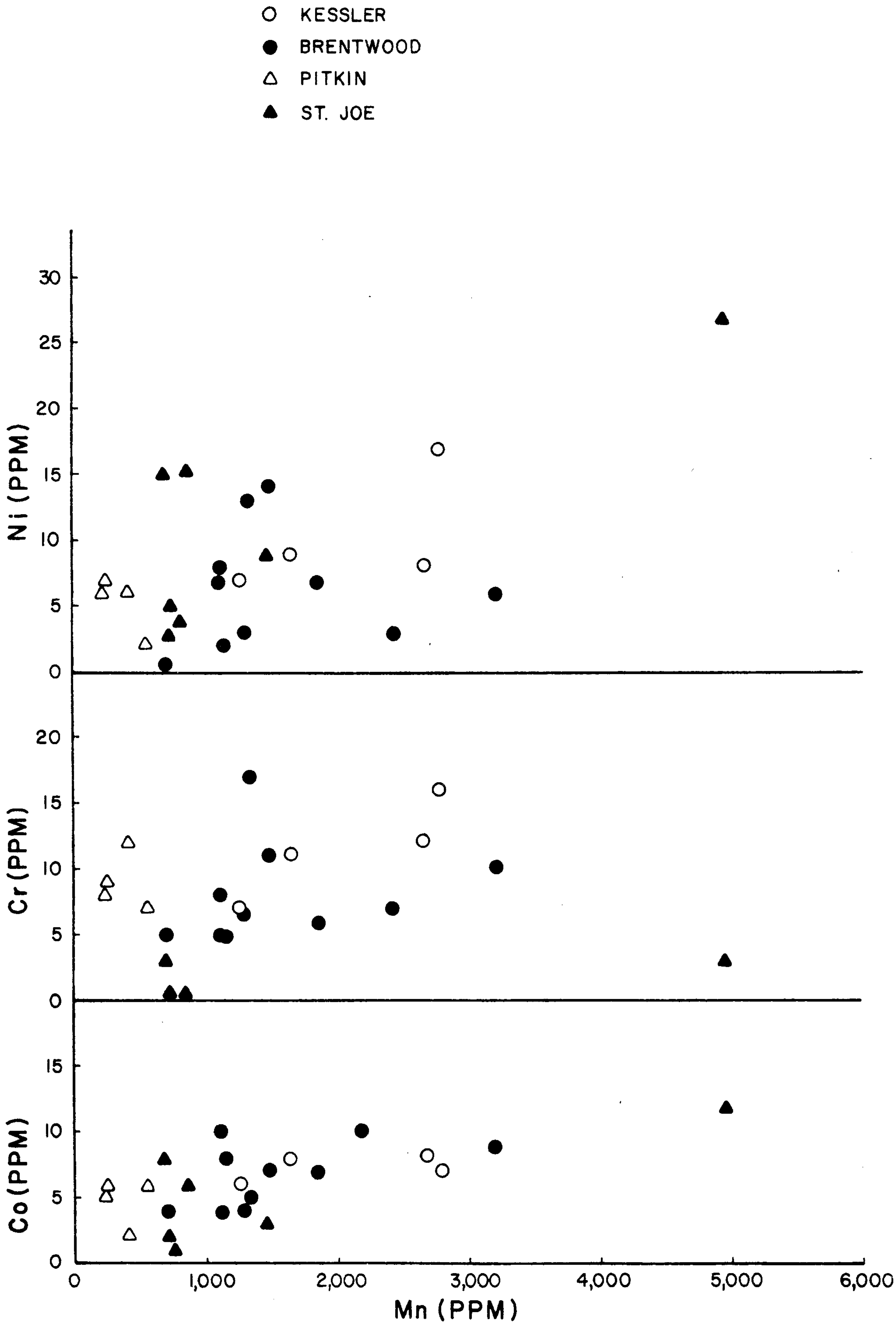

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Ni (PPM)
30
25
20
15
10
5
0
Cr (PPM)
20
15
10
5
0
Co (PPM)
15
10
5
0
0
1,000
2,000
3,000
4,000
5,000
6,000
Mn (PPM)

Figure 13

Co, Cr and Ni Content versus Fe Content for Kessler, Brentwood, Pitkin and St. Joe Limestones

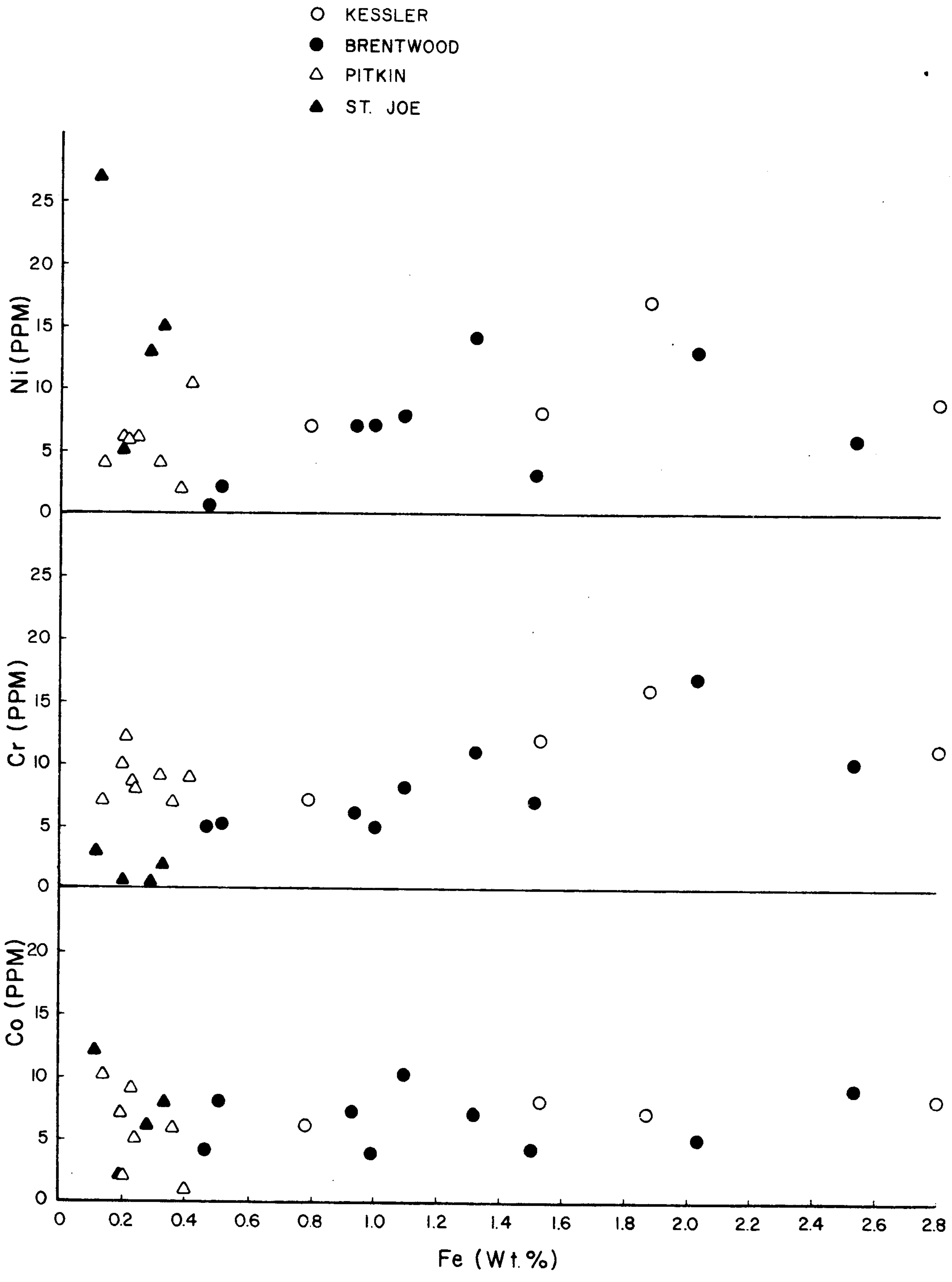
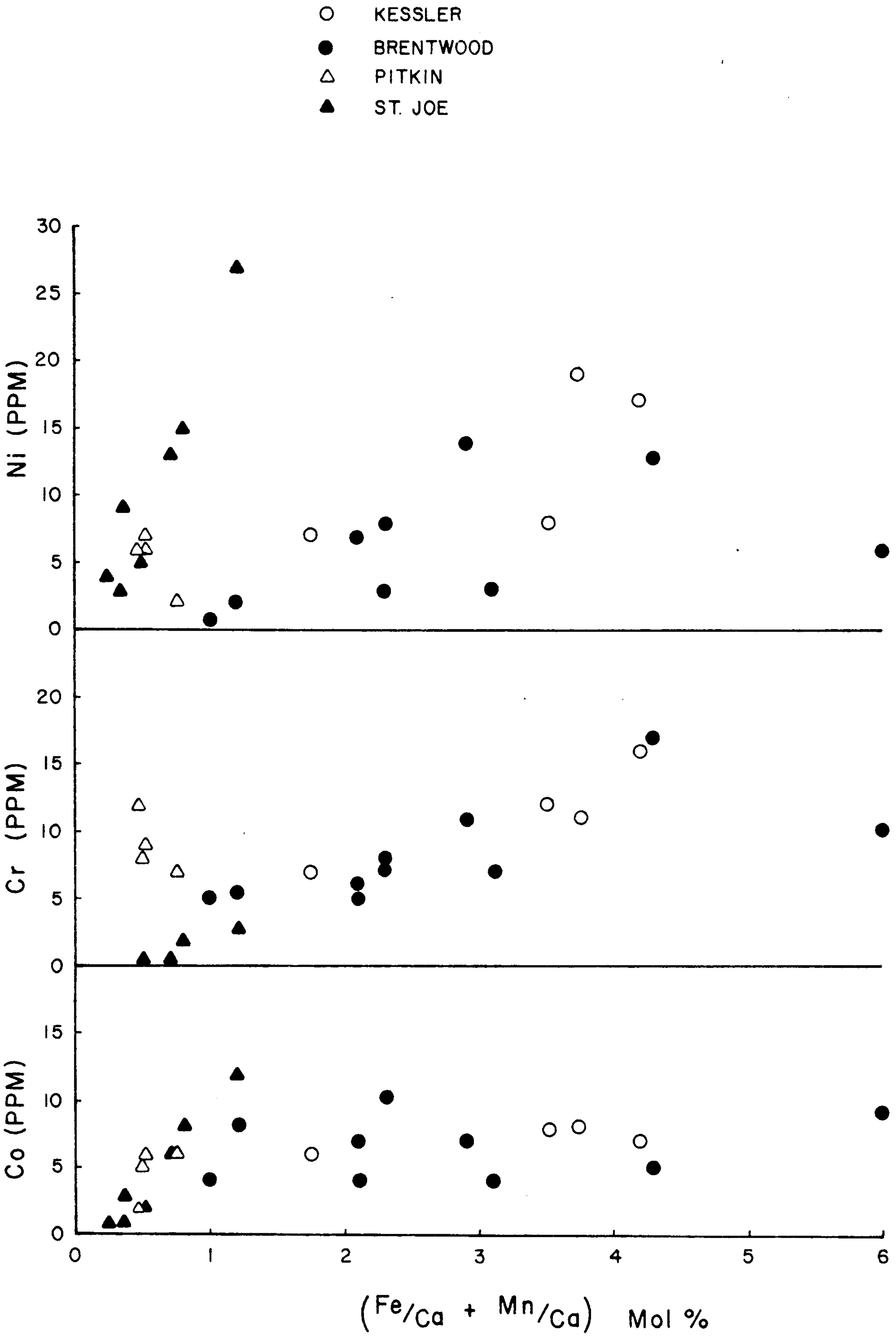

○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Ni (PPM)
25
20
15
10
5
0
Cr (PPM)
25
20
15
10
5
0
Co (PPM)
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Fe (Wt.%)

Figure 14

Co, Cr and Ni Content versus (Fe/Ca + Mn/Ca) for Kessler, Brentwood, Pitkin and St. Joe Limestones


○ KESSLER
● BRENTWOOD
△ PITKIN
▲ ST. JOE
Ni (PPM)
30
25
20
15
10
5
0
Cr (PPM)
20
15
10
5
0
Co (PPM)
15
10
5
0
0
1
2
3
4
5
6
$(\mathrm{Fe}/\mathrm{Ca} + \mathrm{Mn}/\mathrm{Ca})$ Mol %