

## GEOCHEMICAL COMPOSITIONS OF SOME PRECAMBRIAN SHALES FROM THE CANADIAN SHIELD

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### ABSTRACT

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Forty-three elements or constituents have been analysed on eight composites representing 406 samples of Archean (> 2.5 Ga) shale and nine composites of 396 samples of Aphebian (1.6–2.5 Ga) shale. These samples were obtained from 54 localities in, or flanking, the Superior Province of the Canadian Shield.

The composition of the Archean samples reflects their origin as products of the rapid deposition of detritus from terrane that was dominantly volcanic and mafic in composition. By contrast, the Aphebian samples are highly mature and were derived from more “granitic” sources.

The C/S ratio for Aphebian shales is close to 0.36, similar to that of modern sediments, which is consistent with the fixing of S by sulphide-reducing bacteria. Only three of the Archean composites contain significant amounts of C and S and for these samples the elements are closely correlated in the ratio 1 : 1.  $\delta^{34}\text{S}$  values for the Archean composites are close to zero, suggesting a volcanic source. It appears that within Archean greenstone belts the environments most favourable to organic growth and preservation were close to sulphur springs, where sulphur-oxidizing bacteria fixed  $\text{CO}_2$ . These C- and S-rich Archean samples are also enriched in Cu, Zn, As, Ag, Sn, Sb, Hg and Pb, further suggestive of deposition near volcanic springs.

The Aphebian samples have a whole-rock average  $\delta^{34}\text{S}$  of +12‰, quite different from the negative values characteristic of the Phanerozoic and Recent sediments. There is a remarkable peak of Hg in shales of this age. Sedimentary differentiation taking place during Aphebian time has produced both Fe-poor and Fe-rich sediments, including Superior-type iron formation.

### INTRODUCTION

The Archean–Proterozoic boundary marks the most important transition in the development of the continents. The Archean is characterized by elongate volcanic–sedimentary (“greenstone”) belts separated by older, high-grade, metamorphic and plutonic rocks. The crust is believed to have been relatively thin and unstable and its igneous rocks the product of weak fractionation. The

sediments of the greenstone belts are immature, like their more modern analogues of flysch and molasse facies. At the close of Archean time the protocontinents thickened and coalesced to form more stable continental masses. Proterozoic igneous rock series are commonly more strongly fractionated and the sediments on the continents of this age were predominantly of a mature, miogeoclinal type. The transition from Archean to Proterozoic crustal conditions was probably diachronous (Cloud, 1976), but over much of the crust it occurred at  $\sim 2.5$  Ga.

It is apparent that comparison of early Proterozoic and Archean sediments is important, since these rocks will reflect the changes attending continental evolution. But of equal importance is that the sediments will contain evidence of the early stages in the evolution of life.

Limited data have previously been published by Cameron and Baumann (1972), and Cameron and Jonasson (1972) for 406 samples of Archean shale from 153 localities in the Superior Province of the Canadian Shield and for 396 samples of shale of Aphebian age (1.6–2.5 Ga) from 54 localities in or flanking this province. Interest in these data has stimulated the analysis of composites of the samples for a large number of elements. The Archean samples have been drawn into eight composites, representing districts within which the samples were collected. The lower Proterozoic samples have been combined into nine composites, each representing a stratigraphic unit. The locations of the composites are given in Fig.1. A brief description of the geology of the units sampled has been given previously (Cameron and Baumann, 1972; Cameron and Jonasson, 1972). The samples have been variably, but weakly, metamorphosed. Throughout the text they are referred to as shale, to indicate deposition as a sediment of dominantly clay grade.

There are serious problems in obtaining samples that are representative of sediments deposited in Precambrian time. It must be emphasized that the values given here are unlikely to be a true estimate of the composition of Archean or Aphebian shales, even for this restricted portion of the crust. The most fundamental cause for the sampling problems is that the proportion of sediment types of Precambrian age that are now preserved undoubtedly differ from that originally deposited. For instance, most Archean sediments presently exposed in greenstone belts are of "eugeoclinal" type. Only minor thicknesses of the more mature orthoquartzite-carbonate sequences have been discovered. But it is known that there must have been large-scale deposition of carbonate to serve as a sink for Ca (Cameron and Baumann, 1972) and for  $O_2$  (Garrels et al., 1973). For the Proterozoic, the opposite tendency appears to have been effective, with possibly a lesser proportion of eugeoclinal sediments being preserved (Engel et al., 1974).

Added to this fundamental bias influencing the sampling of Precambrian sediments, are the difficulties of representatively sampling the shales that are now preserved in the crust. This lithology is generally recessive, so that shales that outcrop may differ significantly from the total sample. To reduce this source of bias, drill core as well as outcrop samples were taken. But neither are

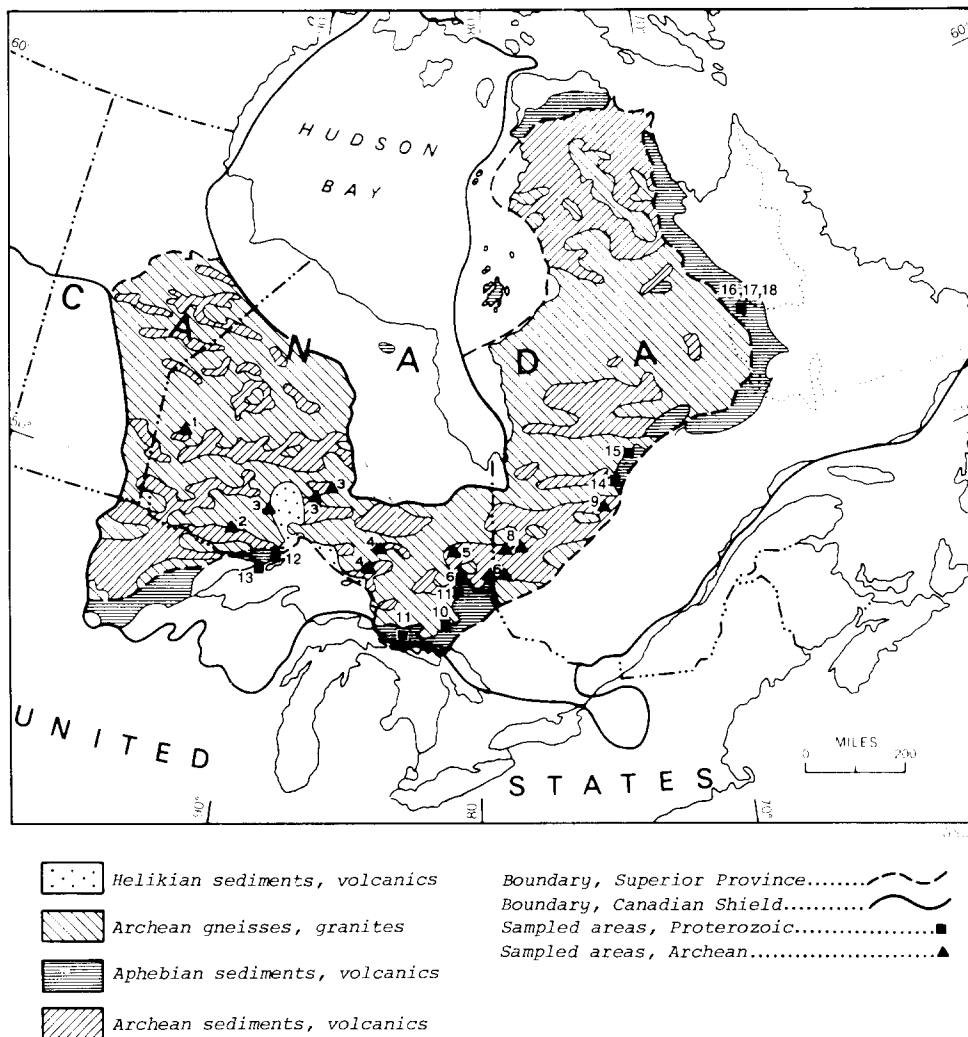


Fig. 1. Sample location map. Location numbers for composites may be referred to Tables I and II.

these a truly random sample, since units were drilled because of a real or presumed association with economic minerals or because they simulated sulphide mineralization (i.e. graphitic shales of low resistivity).

Because of these sampling difficulties, care must be taken in interpreting the data, particularly the average values. For instance, in the case of C in the Archean, the results show that shale units may contain either relatively high or low contents of this constituent. The average value of C given for the Archean sampling reflect the proportions of samples taken from high and low content units: the true distribution of these units is not known.

## ANALYSIS

The composite samples were formed from equal amounts of samples taken from the given locality or unit. Sample preparation has previously been described (Cameron and Jonasson, 1972).

The analyses given are the averages of duplicate analyses by the following methods:

(1) *Si, Ti, Al, Fe, Mg, Ca, Na, K, Mn, P and S.* X-ray fluorescence after fusion with lithium metaborate and lithium tetraborate using ammonium nitrate as oxidizing agent.

(2) *Li, Co, Ni, Cu, Zn, As, Rb, Sb, Hg and Pb.* Atomic absorption spectrometry after decomposition with HF (Co, Ni, Cu, Zn, Pb), with HF—HClO<sub>3</sub> (Li, Rb), with aqua regia (As, Sb), and with HNO<sub>3</sub>—HCl (Hg).

(3) *Be, B, Sc, V, Cr, Ga, Ge, Y, Ag, Sn, Ba, La.* D.C. are spectrochemical.

(4) *Mo.* Zinc dithiol colourimetric after Na<sub>2</sub>CO<sub>3</sub>—KNO<sub>3</sub> fusion.

(5) *Cl.* Mercury thiocyanate—ferric ammonium sulphate colourimetric after Na<sub>2</sub>CO<sub>3</sub> fusion.

(6) *F.* Selective-ion electrode after Na<sub>2</sub>CO<sub>3</sub> fusion.

(7) *S.* Starch iodide titration of SO<sub>2</sub> after ignition.

(8) *CO<sub>2</sub>.* Non-aqueous titration after HCl evolution.

(9) *C.* Ignition with V<sub>2</sub>O<sub>5</sub> + Fe, non-aqueous titration.

(10) *Loss-on-ignition (LOI).* At 850°C.

(11) *H<sub>2</sub>O.* Penfield ignition and Karl Fischer titration.

(12) *U.* Delayed neutron counting.

(13) *S-isotope ratio.* Determined as SO<sub>2</sub> after extraction with HNO<sub>3</sub>—Br mixture by Department of Chemistry, McMaster University, Hamilton, Ontario.

For certain elements the analyses listed in this paper may differ somewhat from those previously reported for the same samples (Cameron and Baumann, 1972; Cameron and Jonasson, 1972). In part, this is because of different analytical methods. The previously quoted data for S, obtained by XRF analysis of ground, unfused, powder are now considered to be unsatisfactory.

## RESULTS

Major-element and S-isotope analyses are given in Table I and minor-element analyses in Table II. The Aphebian samples have been divided into "typical" shales from six localities, comprising 326 samples, and Fe-rich shales from three localities, comprising 70 samples. Only the 326 samples have been included in the Aphebian weighted mean given in Tables I and II and again in Tables III and IV.

*Alkali elements, strontium*

A plot of Na/K vs. Sr/Rb for the composites (Fig.2), illustrates the major differences between the Archean and Aphebian samples. Both ratios decrease

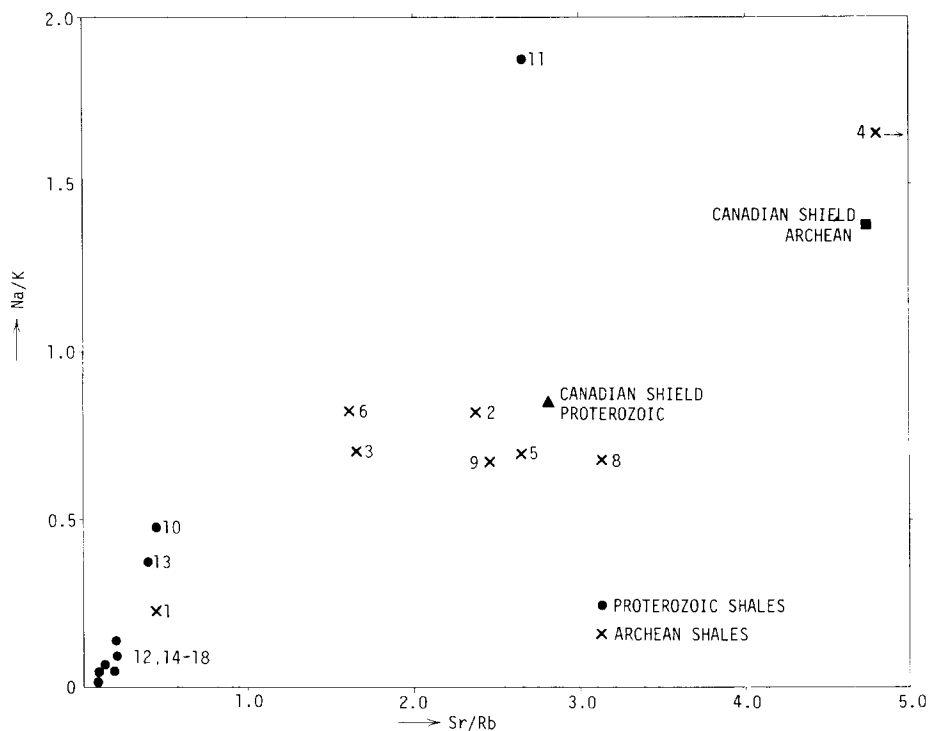


Fig. 2. Plot of Na/K vs. Sr/Rb for Archean and Proterozoic (Aphebian) shale composites. Data on Na, K, Sr for Archean and Proterozoic portions of Canadian Shield from Eade and Fahrig (1971). In absence of Rb data from Eade and Fahrig compilations, Rb calculated as  $K/260$ .

with increasing sedimentary maturity and with increasing differentiation of source igneous rocks. All but one of the Aphebian samples fall in a cluster near the origin, while six of the eight Archean samples are clustered at higher values of both ratios. By reference to the plots for Shield terrane of Archean and of Proterozoic age, it is apparent that the low ratios characteristic of the Aphebian shales is the product of both high sedimentary maturity and more strongly differentiated source rocks.

The one Aphebian composite that is compositionally immature is Gowganda shale (No. 11). This is from a sedimentary sequence believed to be of glacial origin. Archean composite No. 1, from the Red Lake area, is much more mature than the other shales of this age. This is in agreement with the observation (Donaldson and Jackson, 1965) that the sediments of the area are more mature than typical Archean sediments, probably having been derived from a sialic source area. Composite No. 4 has distinctly anomalous ratios.

TABLE I

Major-element analysis (in wt. %) of 806 Precambrian shales from the Canadian Shield

Sample description		SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> <sup>e</sup>	MnO	MgO
<i>Archean:</i>							
(1) <sup>a</sup> Red Lake <sup>b</sup>	12c <sup>c</sup>	56.3	0.65	18.1	10.4	0.15	2.60
(2) Atikokan	27o <sup>d</sup>	59.0	0.70	17.3	7.2	0.09	3.71
(3) Lac des Iles and Beardmore	103o	55.9	0.77	17.8	8.5	0.10	4.43
(4) Michipicoten and Oba	6c/6o	57.2	0.54	12.7	11.7	0.03	1.46
(5) Timmins	110c/31o	59.4	0.69	16.4	6.3	0.08	3.20
(6) Matachewan and Larder Lake and Kenojevis River	67o	57.5	0.83	18.4	8.1	0.09	3.83
(8) Desmeloizes and Amos-Barraute	15o	59.4	0.86	18.3	7.2	0.09	3.44
(9) Chapais	29o	62.6	0.61	16.6	6.2	0.06	2.58
Total	406						
Weighted average		58.0	0.73	16.9	7.6	0.09	3.33
<i>Aphebian:</i>							
(10) Whitewater	16o	59.4	0.90	18.7	6.0	0.04	2.66
(11) Gowganda	24o	58.8	0.81	16.5	7.6	0.13	4.23
(13) Rove	137o	60.7	0.87	17.6	6.7	0.04	2.72
(14) Albanel	2c/36o	67.7	0.54	11.1	3.3	0.01	1.23
(16) Attikamagen	50o	67.0	0.59	13.5	4.4	0.05	1.56
(18) Menihék	61o	62.2	0.55	14.5	7.5	0.13	2.41
Total	326						
Weighted average		62.6	0.73	15.6	6.1	0.06	2.42
<i>Aphebian iron formation:</i>							
(12) Gunflint	46o	54.9	0.43	7.7	21.3	0.15	2.10
(13) Temiscamie	14o	42.2	0.20	5.9	28.2	0.04	5.01
(17) Ruth	10o	51.3	0.91	9.3	20.0	3.92	1.09
Total	70						

<sup>a</sup>composite code; <sup>b</sup>sample localities; <sup>c</sup>number of samples taken from cores; <sup>d</sup>number of samples from outcrops; <sup>e</sup>total Fe as Fe<sub>2</sub>O<sub>3</sub>; <sup>f</sup>loss on ignition.

### Carbon, sulphur, sulphur isotopes

Fig. 3 is a plot of S vs. C. For the Proterozoic samples there is a weak positive correlation between these elements. The ratio S/C = 0.36, as found by Goldhaber and Kaplan (1974) for modern marine sediments from a variety of environments, is a reasonable representation of this correlation. In the case of

CaO	Na <sub>2</sub> O	K <sub>2</sub> O	CO <sub>2</sub>	C	S	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O	LOI <sup>f</sup>	$\delta^{34}\text{S}$ (‰)	
1.08	1.0	4.05	0.0	2.1	2.24	0.07	3.0	5.8	+	1.22
1.54	2.9	3.13	0.6	0.1	0.16	0.20	3.2	3.7	+	0.6
2.17	2.5	3.18	1.1	0.1	0.14	0.17	4.1	4.4	—	
0.64	2.6	1.40	0.0	5.0	4.70	0.10	3.6	12.0	—	0.46
2.61	3.2	2.38	1.5	1.4	1.06	0.14	2.9	5.3	+	1.44
1.39	2.5	3.20	0.9	0.2	0.14	0.19	3.5	4.4	—	
1.42	2.3	2.50	0.6	0.2	0.11	0.16	3.6	4.1	—	
1.44	2.6	3.48	0.8	0.0	0.12	0.19	2.8	3.6	+	2.1
2.07	2.5	2.73	1.1	0.7	0.66	0.16	3.4	4.5	+	1.31 ± 0.32
0.35	2.3	4.24	0.0	1.8	0.05	0.16	3.8	5.7	—	
1.63	4.5	2.18	0.0	0.0	0.10	0.19	3.6	2.9	+	2.4
0.42	1.7	4.05	0.0	0.6	0.21	0.15	4.2	5.1	+	16.5
0.89	0.5	5.38	0.6	5.1	1.84	0.09	1.3	9.0	—	0.34
0.07	0.3	6.95	0.0	2.0	0.94	0.07	3.0	6.2	+	13.61
0.40	0.7	4.76	0.3	2.0	0.94	0.12	3.9	6.5	+	10.99
0.50	1.4	4.65	0.1	1.6	0.63	0.13	3.6	5.9	+	11.79 ± 4.37
1.18	0.1	1.86	1.7	0.3	0.98	0.32	5.4	9.9	+	6.18
1.83	0.2	2.80	7.0	2.0	0.62	0.19	3.6	12.9	+	15.8
0.13	0.0	4.44	0.2	1.1	0.09	0.15	6.0	8.6	—	

modern sediments the correlation between C and S is due to sulphate-reducing bacteria consuming organic matter. These bacteria oxidize approximately 20% of deposited organic matter, measured as C, to produce sulphide (Berner, 1970; Goldhaber and Kaplan, 1974).

The S-isotope data for Aphebian composites (Table I) also suggest that bacterial reduction of sulphate has taken place. S in these samples is believed

TABLE II

Minor-element analysis (in ppm) of 806 Precambrian shales from the Canadian Shield

Compo- site code <sup>a</sup>	Li	Be	B	F	Cl	Sc	V	Cr	Co	Ni	Cu	Zn	Ga
<i>Archean:</i>													
1	43	3.6	70	400	400	21	150	141	45	147	87	195	21
2	57	3.5	7	500	100	15	130	119	30	91	47	96	16
3	51	3.3	30	400	100	19	150	147	35	125	59	100	14
4	18	2.9	10	300	100	9	75	55	35	82	99	435	17
5	27	2.5	30	400	100	15	110	130	38	147	82	702	16
6	61	3.2	50	400	100	18	150	168	35	140	52	114	17
8	49	3.4	30	300	200	18	150	140	30	120	48	102	22
9	28	3.1	20	400	100	12	110	62	20	52	56	93	18
Weighted average	42	3.0	33	400	100	16	130	133	35	127	66	323	16
<i>Aphebian:</i>													
10	69	3.4	20	700	100	17	130	147	17	69	67	78	25
11	44	5.4	5	300	100	19	210	104	30	82	40	108	17
13	85	4.0	30	700	200	20	170	145	19	69	70	173	23
14	17	3.8	20	300	200	9	89	60	69	61	222	17	19
16	41	4.5	30	1,500	100	10	240	68	8	25	30	47	14
18	50	5.4	20	1,200	100	13	260	63	11	41	50	111	20
Weighted average	60	4.4	25	840	150	16	188	105	22	57	75	114	20
<i>Aphebian iron formation:</i>													
12	67	4.6	20	300	200	9	170	48	14	22	34	36	13
15	25	3.9	30	700	200	7	130	26	6	13	10	42	7
17	79	8.4	10	1,400	100	11	330	43	20	22	26	47	15



TABLE II (continued)

Compo- site code <sup>a</sup>	Ge	As	Rb	Sr	Y	Mo	Ag	Sn	Sb	Ba	La	Hg <sup>b</sup>	Pb	U
<i>Archean:</i>														
1	0.3	32	112	50	16	2.0	0.17	3.8	1.1	470	21	81	13	1.7
2	0.3	23	117	280	18	5.0	0.08	1.5	0.9	730	26	69	13	2.3
3	0.3	17	113	190	18	3.5	0.06	1.4	1.2	600	25	151	12	2.1
4	1.5	75	43	530	14	4.0	0.19	5.9	5.9	320	25	241	12	1.3
5	0.3	73	68	180	18	2.0	0.95	6.2	1.4	460	21	206	51	1.4
6	0.3	61	99	160	21	1.5	0.14	1.4	0.7	680	28	94	16	1.7
8	0.7	13	73	230	22	1.0	0.10	1.9	0.3	510	21	67	12	1.3
9	0.3	18	99	240	11	0.5	0.10	1.2	0.1	560	22	73	14	1.8
Weighted average	0.3	46	91	199	18	2.2	0.40	3.28	1.2	550	24	147	26	1.7
<i>Aphebian:</i>														
10	0.3	17	190	90	23	10.0	0.26	2.3	3.4	850	23	618	12	8.6
11	0.3	5	94	250	22	1.0	0.10	1.7	0.1	430	29	126	48	3.3
13	2.7	14	178	70	26	6.0	0.46	2.8	0.9	610	37	299	22	6.5
14	0.3	81	134	30	19	2.0	0.35	2.0	0.4	2,100	73	360	12	4.2
16	1.7	21	211	40	23	4.5	0.31	2.1	1.4	450	48	585	23	5.1
18	1.5	19	188	40	34	6.0	0.56	3.5	2.8	500	45	719	20	7.0
Weighted average	1.7	23	174	69	25	4.5	0.41	2.6	1.3	492	43	431	22	5.9
<i>Aphebian iron formation:</i>														
12	2.8	57	56	10	28	12.5	0.08	1.1	0.6	220	33	611	12	5.9
15	9.4	13	129	20	23	1.0	0.05	8.5	0.3	180	36	475	11	1.1
17	9.7	49	188	20	88	12.5	0.16	5.4	0.1	400	140	815	12	10.8

<sup>a</sup>Composite code from Table I; <sup>b</sup>Hg in ppb.

TABLE III

Comparison of the major elements in shales for the Archean, Aphebian and Phanerozoic

	Archean <sup>a</sup>	Aphebian <sup>a</sup>	Phanerozoic <sup>b</sup> (carbonate-free)	Phanerozoic <sup>b</sup> (with carbonates)
SiO <sub>2</sub>	60.52	65.00	63.11	60.02
TiO <sub>2</sub>	0.76	0.76	0.89	0.85
Al <sub>2</sub> O <sub>3</sub>	17.63	16.22	18.80	17.88
Fe <sub>2</sub> O <sub>3</sub>	7.91	6.37	7.79	7.42
MgO	3.47	2.51	3.11	2.96
CaO	2.16	0.52	0.07	4.96
Na <sub>2</sub> O	2.62	1.44	1.27	1.21
K <sub>2</sub> O	2.84	4.83	3.69	3.51
C	0.77	1.68	0.87 <sup>c</sup>	0.83 <sup>c</sup>
S	0.66	0.65	0.38 <sup>d</sup>	0.36 <sup>d</sup>
δ <sup>34</sup> S (‰)	+1.31 ± 0.32	+11.79 ± 4.37	-12 <sup>e</sup>	-12 <sup>e</sup>
Total	99.98	99.98	99.98	100.00

<sup>a</sup>From Table I. Recalculated to 100% by weight.<sup>b</sup>From Ronov and Yaroshevsky (1967) and Wedepohl (1969), except where otherwise noted. Numbers represent unweighted average of Ronov and Yaroshevsky (1967), average platform shale and average geosynclinal shale, and Wedepohl (1969), average platform shale and average geosynclinal shale. Column recalculated to 100%.<sup>c</sup>Ronov and Yaroshevsky (1967), Wedepohl (1969), Ronov and Migdisov (1971).<sup>d</sup>Wedepohl (1969), Ronov and Migdisov (1971).<sup>e</sup>Holser and Kaplan (1966).

to be mainly in the form of pyrite. However, with one exception, the values of δ<sup>34</sup>S are positive and are thus quite different from the <sup>32</sup>S-enriched sulphide of modern marine sediments and the pyrite of shale. Holser and Kaplan (1966) give an average value of δ<sup>34</sup>S = -12‰ for the pyrite of Phanerozoic shale. It is the preferential fixing of <sup>32</sup>S in sediments that has caused the enrichment of <sup>34</sup>S in the modern (δ<sup>34</sup>S = +21‰) and ancient oceans.

There is some evidence that <sup>34</sup>S was also enriched in the Proterozoic oceans. For this period Claypool et al. (1972) gives δ<sup>34</sup>S = +18‰. On the basis of the isotopic composition of sedimentary barite, approximately 1.6 Ga in age, from the middle Proterozoic of northern Australia, Smith et al. (1978) suggest that:

“a considerable reservoir of ocean sulphate with δ<sup>34</sup>S value of + 25 ± 5‰ was available.”

Assuming similar values were characteristic of the Aphebian, it would be possible to produce pyrite with δ<sup>34</sup>S similar to the Aphebian shale average of +12‰ (Table III) as the end product of bacterial reduction of ocean sulphate. This would imply a lesser degree of fractionation than existed, on average, during the Phanerozoic [for a discussion of the mechanisms influencing frac-

TABLE IV

Comparison of minor elements in shales for the Archean, Aphebian and Phanerozoic

Trace element <sup>a</sup>	Archean <sup>b</sup>	Aphebian <sup>b</sup>	Phanerozoic <sup>c</sup>
Li	42	60	74
Be	3.0	4.4	2.9
B	33	25	116
F	400	840	760
Cl	100	150	140
Sc	16	16	13.5
V	130	188	174
Cr	133	105	90 <sup>d</sup>
Co	35	22	19 <sup>d</sup>
Ni	127	57	68 <sup>d</sup>
Cu	66	75	35
Zn	323	114	100
Ga	16	20	23
Ge	0.35	1.7	2
As	46	23	13
Rb	91	174	164
Sr	199	69	194 <sup>e</sup>
Y	18	25	30
Mo	2.2	4.5	2.6 <sup>d</sup>
Ag	0.4	0.41	0.16
Sn	3.28	2.6	4
Sb	1.2	1.3	1.5
Ba	550	492	546
La	24	43	92 <sup>d</sup>
Hg	0.147	0.431	0.04 <sup>f</sup>
Pb	26	22	21.6
U	1.7	5.9	3.7 <sup>d</sup>

<sup>a</sup>Numbers given in ppm; <sup>b</sup>from Table II; <sup>c</sup>Wedepohl (1969, 1970, 1972, 1974); <sup>d</sup>Turekian and Wedepohl (1961); <sup>e</sup>Rheimer (1972); <sup>f</sup>Fleischer (1970), Cameron and Jonasson (1972).

tionation, see Goldhaber and Kaplan (1974)], or deposition in a basin with greater <sup>34</sup>S enrichment than the ocean of the day. However, whatever the explanation, a problem of considerable interest remains: the locus of the excess <sup>32</sup>S of Proterozoic time to balance the excess <sup>34</sup>S present in these shales and in the oceans. The conclusions derived from these whole-rock isotopic data must be considered preliminary until more detailed analyses of the Aphebian shales has confirmed that pyrite does indeed dominate the S-isotope geochemistry of these rocks.

While S-isotope data on Proterozoic sediments are rather scant, pyrite from the shale-hosted base metal deposits of Mt. Isa (Smith et al., 1978), Lady Loretta (Carr and Smith, 1977) and McArthur (Smith and Croxford, 1973) show consistently positive values of  $\delta^{34}\text{S}$ , averaging +16, +12 and +6‰, respec

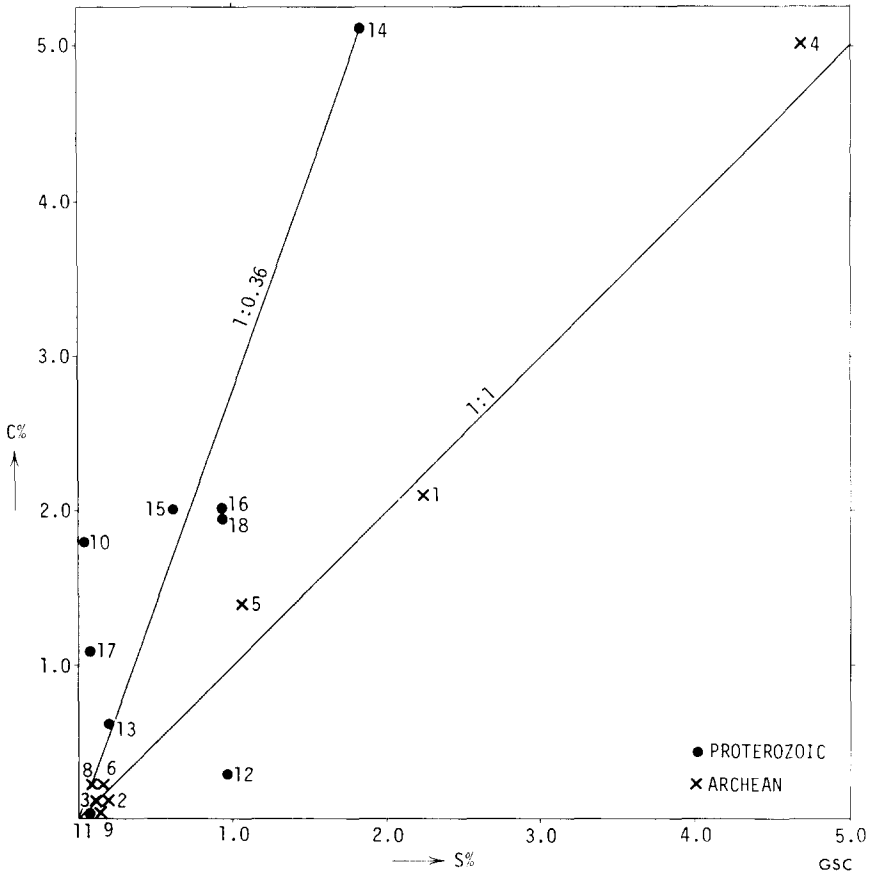


Fig. 3. Plot of C vs. S for Archean and Proterozoic (Aphebian) shale composites.

tively. All are from the Northern Territory Australia and have an approximate age of 1.6 Ga. Sedimentary barite, at the stratigraphic top of the Lady Loretta ore horizon has a  $\delta^{34}\text{S}$  composition of  $\sim +39\text{‰}$ .

The C and S data for the Archean samples are substantially different from that of the Proterozoic shales. Values for  $\delta^{34}\text{S}$  are consistently close to zero for all composites measured. Thus, it is unlikely that this sulphide was formed by bacterial reduction of sulphate. This is in agreement with the observations of Perry et al. (1970) who found little fractionation between sulphate and sulphide samples of Archean age. They suggest that at this time, when the atmosphere lacked  $\text{O}_2$ , sulphate occurred in insufficient quantities for fractionation to be effective. Donnelly et al. (1977) have recently reported an average  $\delta^{34}\text{S} = +1.6\text{‰}$  for sulphides from sedimentary rocks of Archean age from Western Australia.

The majority of the Archean composites contain little C or S (Fig.3, Table I). But three samples have relatively large amounts of these elements in pro-

portions close to 1 : 1. These data suggest that environments within which C and S could be deposited were more limited in extent in Archean time than during the Proterozoic and also, that the deposition of either C or S was dependent on the other. But the S-isotope data indicate that the relationship between these elements is not the same as for modern sediments, i.e. bacteria utilizing C to fix S.

In the Archean greenstone belts of the Canadian Shield graphitic sediments often occur within or near to volcanic sequences and, more specifically, are frequently related stratigraphically to the sites of volcanic exhalations. Indeed, graphitic units provide numerous false targets during the electromagnetic exploration of greenstone belts for massive sulphide mineralization. Zn is the most common base metal of volcanic exhalative mineralization. Archean shale composites with low contents of S (and C) contain similar and low amounts of Zn, near to 100 ppm (Fig.4). But the samples with > 1% S (and similar amounts of C) contain much greater amounts of Zn. The same tendency is not evident in the Proterozoic samples. These results suggest that the Archean composites with > 1% S derived this S and much Zn from nearby volcanic springs, whereas this was not the case for the Proterozoic composites with significant amounts of S. The association of C with S in the Archean samples may be because the sites where volcanic exhalations entered the sea were particularly suitable for organic growth. One type of organism that might have flourished in this environment are bacteria that utilize the oxidation of S compounds. A

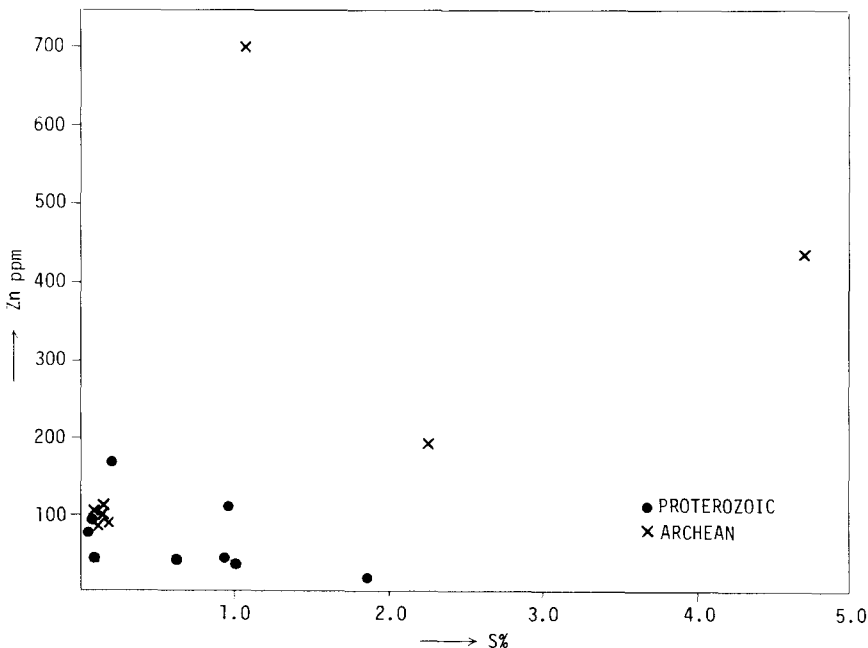


Fig.4. Plot of Zn vs. S for Archean and Proterozoic (Aphebian) shale composites.

variety of chemosynthetic and photosynthetic bacteria are known to utilize the energy derived from the oxidation of reduced S compounds to fix  $\text{CO}_2$ .

### Trace elements

The distribution of trace elements in the shale composites appears to be governed by three important factors: the presence or not of material of volcanic exhalative origin; the derivation of Archean samples from more strongly differentiated igneous rocks; and the greater maturity of the Archean samples.

Archean composites Nos. 1, 4 and 5 are all S-bearing and one or more are richer in Cu, Zn, As, Ag, Sn, Sb, Hg and Pb than the S-poor sediments. These elements are characteristic of the massive sulphide mineralization of greenstone

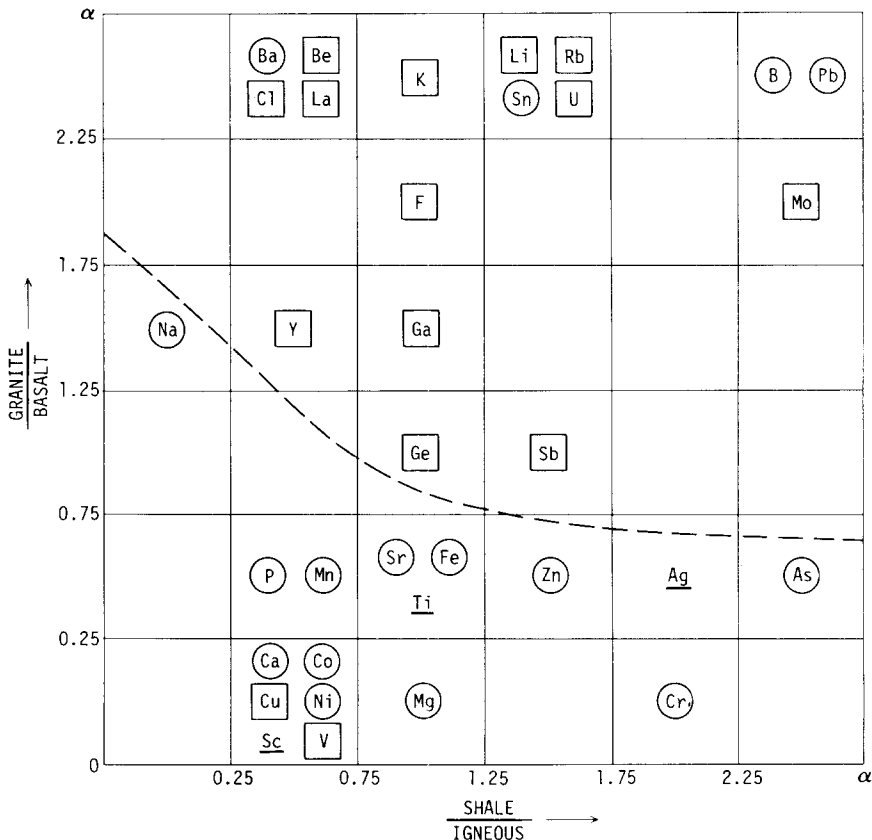


Fig. 5. Relative abundance of elements in Archean and Proterozoic (Aphebian) shale composites on basis of their distribution between granite and basalt (Taylor, 1964) and between shale and igneous rock (Horn and Adams, 1966). Circles: elements more abundant in Archean composites; squares: elements more abundant in Aphebian composites; line: equal abundance (all calculated from weighted means, Tables III and IV).

belts. It is suggested that the excess contents of these elements, and the S, were derived from volcanic exhalations.

In Fig. 5, elements are plotted in terms of their distribution between granites and basalts and also in terms of their distribution between igneous rocks and shales. The former ratio is a guide to those elements that were likely more abundant in Proterozoic than in Archean igneous rocks. The shale/igneous ratio reflects the tendency for loss or retention of elements from the solid products of weathering and also the supply of some elements as volatiles (e.g., B). The figure shows that those elements that are, on average, more abundant in the Archean composites are those that are enriched in mafic rocks (e.g., Mg, Ni); or are supplied from volcanic exhalations (e.g., As, B); or are more susceptible to loss during weathering (e.g., Na). Note that the greater average quantities of the lithophile elements Pb and Sn in the Archean composites are entirely due to their abundance in one or more of the sulphide-bearing samples.

Other features of note (Tables I and IV) are the very low Ca, Sr and CO<sub>2</sub> contents of the Aphebian composites, indicative of an almost complete separation of silicate and carbonate sedimentation; the high levels of Hg in the Aphebian samples (Cameron and Jonasson, 1972); and the low contents of B in Precambrian shales compared to the Phanerozoic. Note that the average Fe content of the Aphebian shales is lower than either the Archean or Phanerozoic average values (Table III). This depletion is most strongly expressed in the Al-banel and Attikamagen composites — shales that come from sedimentary sequences containing iron formation. This suggests that sedimentary differentiation taking place during Aphebian time produced Fe-poor and Fe-rich sediments, the latter probably including Superior-type iron formation.

### *Iron-rich Aphebian composites*

The shales associated with the Proterozoic iron formations (composites Nos. 12, 15 and 17) are distinctive in their much higher Fe content and the major quantities of Mn in No. 17. The very low amounts of Na and Sr indicate that the clastic component of these shales is exceptionally mature. The dilution of this component by Fe and Mn minerals hinders comparison with other Aphebian shales. But when compared on a constant Al basis, the Fe-rich samples are, on the average, depleted in elements associated with mafic rocks, e.g. Cr, Cu, Ni, Zn and Ag, and are more abundant in Mo, P, As, Hg, Y, Cl, S, Sn, Be, La, Mg, Li, V, U and B. The apparent enrichment of the latter elements may reflect the composition of the clastic component or, alternatively, may be caused by an association of some elements with the Fe or Mn minerals. The elements Y and La are particularly abundant in the manganiferous sample. Overall, these Fe-rich shales are even more mature and the element content has a more strongly lithophile character than the other Aphebian samples.

## CONCLUSIONS

The compositions of the Archean shales are consistent with their being the products of the rapid deposition of weathering products of typical Archean source materials. The source was earlier estimated to comprise 25% sialic and 75% volcanic material; the volcanics being composed of two parts mafic and one part salic rock (Cameron and Baumann, 1972). In addition, some samples show a significant contribution of S and other elements from volcanic exhalative sources.

The Aphebian composites were derived from a more "granitic" source and are more mature than the Archean samples. They are even more mature than the average Phanerozoic shale, indicative of the stable shelf environment in which they were formed. The maturity of these sediments is consistent with the high degree of sedimentary differentiation required to separate Fe from the clastic components of rock weathering and thus to produce iron formation.

The Archean S-isotope values, consistently near to zero for  $\delta^{34}\text{S}$ , are suggestive of a volcanic source for this element. There is an excellent correlation between C and pyritic S, but the proportions of these elements in the Archean samples is much different from Proterozoic, Phanerozoic, or modern samples. It is suggested that this correlation may be the result of volcanic  $\text{H}_2\text{S}$  or other reduced S compounds being used by S-oxidizing bacteria. This is quite different from the correlation between C and S in Proterozoic and later sediments that was caused by sulphate-reducing bacteria utilizing C to produce sulphide. In terms of organic productivity, hot sulphur springs of Archean time may have been the equivalent of today's tropical rain forest. It appears that Archean shales deposited near the springs contain moderate to large amounts of C and S plus a variety of base metals and other elements of volcanogenic derivation. Shales remote from these sources are generally low in these elements.

The strongly positive whole-rock values of  $\delta^{34}\text{S}$  for the Aphebian rocks, contrasted with the strongly negative values for the sulphide of Phanerozoic sediments, is perhaps the most puzzling aspect of all the data given.

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