SEDIMENTS DERIVED FROM THE WEATHERING OF A PRIMORDIAL ANORTHOSITIC CRUST

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY THOMAS ALVIN TEST 1976



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ABSTRACT

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by

Thomas Alvin Test

The sedimentary suite that would be derived from the weathering of a primordial anorthositic crust is estimated using the mass balance equation: Primordial Crust + Primitive Sea = Sediments + Seawater. The derived suite contains approximately 55% potassium-free claystones, 23% limestone, 20% aluminum-rich sediment and one to two percent each evaporites and carbonate-rich iron formation. This suite does not resemble modern sediments, nor does it resemble ancient sediments of appropriate age and tectonic setting to represent the weathering products of a primordial continental crust. Lithologies of these oldest rocks of sedimentary origin suggest a primordial crust of more granitic composition.

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A THESIS

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INTRODUCTION

The early history of the earth's crustal development persists as an unresolved question in geology. Evidence of the nature and evolution of the early crust is infrequent and complex, so that models describing a primordial crust are as varied as they are numerous. One of these models is examined here.

The Model

The model investigated in this study is one of an anorthositic primordial crust, as proposed by D. M. Shaw (1975).

"Following accretion, core separation and ensuing cooling must have been completed in about 0.7 By (earth age 4.55 By) in order for rocks dated at 3.7-3.9 By (Greenland, Minnesota) to develop and be preserved.

"This early history is divided into <u>Prearchean</u> and <u>Protoarchean</u> stages. The first comprised the major earth differentiation into core, peridotitic lower mantle, and basalt upper mantle: this stage terminated in the development of a thin worldwide anorthositic crust. It was followed by condensation of hot acid rains, draining to form shallow intracontinental seas.

"Mantle convection aided rupture of crustal flakes along thermal buckles. Archean greenstone belts appear to represent weld sutures, building wider and thicker continental masses, complemented by wider and deeper basins, leading to present-day plate tectonics."

The early differentiation of the earth and the formation of an igneous global primordial crust is strongly suggested by interplanetary analogy, while the direct terrestrial evidence, mostly isotopic, remains ambiguous (Lowman, 1976).

An anorthositic composition for the primordial crust of the earth is suggested by analogy to lunar crustal composition. Windley (1970) has proposed that certain layered calcic anorthosites in very early Archean high-grade metamorphic terrains, which are chemically quite similar to lunar highland anorthosites, may be tectonically emplaced reworked fragments of a primordial continental crust. No ancient igneous rocks have been located, however, that can be convincingly identified as remnants of the earth's first crust.

Other lines of evidence indicate that the composition of the earth's first crust was probably not anorthositic. As older and older igneous rocks are identified, they are found to be both widespread in cratonic areas and granitic in composition (Hart and Goldich, 1975). This suggests the primordial material might be better characterized as acidic or intermediate in composition. The oldest yet known igneous rocks, in Greenland, range in composition from granite to quartz diorite (McGregor and Bridgwater, 1973; and Bridgwater et al, 1974). These intrude yet older rocks of sedimentary origin, which may provide better clues as to the composition of the primordial crust.

A Sedimentological Approach

The setting provided by the model suggests that the question of the composition of the primordial crust may be investigated from a sedimentological approach, in lieu of direct evidence from remnants. The interaction of shallow intracontinental acid seas with a bare igneous crust

would result in rapid weathering until the seas were neutralized to a chemistry approximating present seawater. The weathered material would be deposited as sediments of types in approximate chemical equilibrium with the neutralized seas. If the primordial crust was not totally destroyed by subduction, some portion of these first continental sediments could be preserved, and would indicate the nature of their primordial source. They would at least impart something of their chemical nature to subsequent sedimentary rocks.

The oldest known rocks on earth are 3700 to 3900 million year old metasediments on the Greenland craton (Moorbath et al, 1973). According to the timetable of Shaw's model, these are of sufficient age to have been derived from the weathering of the first igneous crust, and their existence suggests a sedimentological approach is reasonable.

The approach used in this examination of the suggested anorthositic primordial composition is one of chemical mass balance between the sediments and their source rocks. In principle, it is an application of the law of conservation of mass. When a mass of igneous rock of specified composition is weathered to produce an assortment of sedimentary rocks, the chemical composition of the total mass of sediments must be the same as the composition of the source material, less the constituents that have remained in solution.

When the chemical composition of calcic anorthosites is compared to estimates of the average composition of sedimentary rocks on earth, or to estimates of the earth's average crustal composition, some qualitative differences are apparent. The ratio of SiO_2 to Al_2O_3 in anorthosites is on the order of 1.6 to 1, while this ratio is approximately

4.3 to 1 for averages of either sedimentary rocks or the crust as a whole. In addition to this substantial excess of aluminum with respect to silicon when compared to average sediments, anorthosites have a substantial deficiency of potassium and an excess of calcium. These discrepancies are confirmed by the mass balance calculations in this study.

The chemical mass balance calculations for this study consider the weathering of an anorthositic crust by primitive acid seas to produce common sedimentary rock types. The calculations include the chemical compositions of the initial and final seas, in addition to those of the rocks, in order to include in the mass balance those constituents from the weathered rocks that remain dissolved in the seas, and those components now in sediments that would have originated with the volatiles that formed the primitive seas. The balance equation is as follows:

Primitive Sea + Primordial Crust = b_1 Sediment type 1 + b_2 Sediment type 2 + . . . + b_k Seawater.

The coefficients for the sedimentary rock types derived from this calculation provide an estimate of the proportions of the sedimentary rock types that would result from the weathering of the specified primordial crustal material. This is a suite of sedimentary lithologies that may be compared to ancient sedimentary suites to evaluate the specified crustal material as their source.

This investigation also considers the effect of sedimentary recycling on the sediment derived from a primordial crust. Studies of ages and amounts of exposed sedimentary rocks indicate that a substantial proportion of the sediments deposited at any time are derived from previous sedimentary rocks, and that the older a sedimentary rock, the less

remains of the mass of material originally deposited (Garrels and MacKenzie, 1971; Garrels et al, 1972; and Blatt and Jones, 1975). This observation has some implications important to the present study.

The rate of sedimentary recycling will determine the probability of finding a very ancient sedimentary rock. Estimates of recycling rates predict that sedimentary rocks of near primordial age may still exist, but would be rare.

Differential rates of recycling, whereby more soluble types of sedimentary rocks are less well preserved, are are weathered and redeposited more frequently, would alter the proportions of rock types in sediments of a given age. It may be inferred that older sedimentary rocks may have originally had greater proportions of the more soluble lithologies, such as evaporites and carbonates, than are represented by their modern exposures. The effects of differential recycling are generally predictable.

Sedimentary recycling will also impart some of the chemical character of earlier sedimentary rocks to subsequent sediments. This effect is evaluated in this study.

THE CHEMICAL MASS BALANCE TEST

The sedimentary suites that would be derived from the weathering of a primordial anorthositic crust are estimated with a chemical mass balance equation as follows:

Primitive acid seas + Primordial crust = b_1 Sediment type 1 + b_2 Sediment type 2 + . . . + b_k Seawater.

The primordial crust, primitive sea, sedimentary rock types, and final

seawater are characterized by the mass proportions of their chemical components, so that there is a linear balance equation for each component considered. A least squares regression procedure is used to estimate the b coefficients for the sedimentary rock types from the set of linear balance equations, so that the masses of the components on each side of the equation are balanced. This estimate can be compared to ancient sedimentary suites that may represent the weathering products of the proposed primordial crust.

Method of calculation.

The method used to calculate this mass balance is the least squares approximation method, using high speed computers, developed by Bryan et al (1968) for estimating proportions in petrographic mixing equations. This method has been applied to sedimentary chemical mass balance equations by Sibley and Vogel (1976).

The computer program is a multiple regression procedure whereby the b values, the least squares estimates of the regression coefficients, in this case the coefficients for the sedimentary rock types, are obtained from a set of equations X'Xb = X'Y by matrix manipulation such that $b = (X'X)^{-1}(X'Y)$. The method requires that the system analysed has a number of independent equations (number of components characterizing a rock type), n, equal to or greater than the number of parameters to be estimated (number of b coefficients to be generated), k. This study meets this requirement for all estimates calculated.

The program places an additional constraint on the system in the least squares solution of the predicted value of a constituent in the parent, or source rock, Y, from the regression equation:

 $Y = A + b_1 X_1 + b_2 X_2 + . . . + b_k X_k.$

This constraint consists of forcing the equation through the origin, so that the intercept A is zero. This is achieved by eliminating the first row and column of the X'X matrix and the first terms of the b and X'Y column vectors to form reduced matrices.

While predictions of small numbers are more error prone using reduced matrices than using nonreduced matrices, and care is required in the interpretation of the significance of small numbers produced, a test of the method by comparison with regressions calculated using nonreduced matrices (Sibley and Wilband, 1977) indicates that the Bryan et al method is as good a predictor of b values (regression coefficients) as more conventional regression techniques so long as the values of the sums of squares of residuals (SSR) are low. Forcing the equations through the origin does not significantly alter the b values for those regressions providing a good fit, whether derived on reduced or nonreduced matrices. The geological ambiguity implied by nonzero intercepts is avoided when the Bryan et al method is used.

CHOICE OF MATERIALS FOR THE MASS BALANCE CALCULATIONS Sedimentary rock types.

Where possible, the compositions for the sedimentary rock types were obtained from widely available published data, with a preference for data previously used in chemical mass balance calculations. The chosen pelagic red clay was selected for its low carbonate content to represent pre-Mesozoic pelagic sediments. Clarke's (1924) average shale, average Paleozoic shale, and average Cenozoic-Mesozoic shale were selected in order to independently evaluate the balance with chemically different shale

types. Averages of Grout's (1933) analyses of Knife Lake lutites and graywackes were selected to determine possible balance differences with Archean sediments; these are well described geologically and are among the oldest on the North American shield. Smectite analyses were obtained from Grim (1968), to represent low potassium clays. Iron formation compositions were selected from Archean types to provide a range of variation of composition.

The chemical compositions for the materials used in the balance calculations are recalculated so that all iron species appear as grams elemental iron per 100 grams rock. Similarly, all carbon species are recalculated as grams CO_2 , and sulfur species as SO_3 . Mass balance can be thus calculated for these elements without concern for the evolution of their oxidation states through geological time as a result of biological and chemical processes. Compositions are not recalculated to 100%. The tabulated component proportions represent the number of grams of the component in the tabulated form that would be derived from all forms of the material in 100 grams of rock.

Elements such as manganese and phosphorous, which occur in very small proportions in all the materials used in the balance calculations, were not used in the calculations. Their abundances are so small that their contributions to the predicted coefficients are insignificant relative to the effect of the major constituents.

Component proportions for the sedimentary rock types used in the mass balance calculations are listed in Table 1.

Final seawater.

The final seawater composition used for the mass balance calculations is that of modern seawater. Some investigators have estimated

Table 1.	Compone	ent propc	ortions	of sedime	entary	rock types	used ir	ı mass ba	lance ca	lculatio	.su	
Component	SS	GW	GWKL	SHAV	SHCM	HS	SHKL	PRC	MONT	SAP	INON	SEA
510,	77.6	66.7	62.4	58.1	55.4	60.2	60.9	53.9	51.47	47.4	43.0	1 1 1
A1,03	7.1	13.5	15.2	15.4	13.8	16.4	17.8	17.46	19.55	10.0	7.71	1 1 1
не г	2.4	3.8	4.0	4.8	4.3	5.1	4.5	6.3	2.09	0.70	18.75	1 1 1
MgO	1.2	2.1	3.5	2.4	2.7	2.3	3.5	4.56	3.73	25.4	0.95	0.21
CaO	3.1	2.5	4.6	3.1	6.0	1.4	2.8	1.56	1.74	1.35	06.0	0.06
Na,0	1.2	2.9	2.7	1.3	1.8	1.0	2.65	1.27	0.66		0.04	1.46
, е Н , о	2.1	4.4	1.6	5.0	5.6	4.7	2.04	6.3	19.65	14.65	18.17	98.3
.00,	2.5	1.56	1.3	5.5	7.2	4.8	1	6.0	1 1 1		! ! !	0.01
1 1	8 1 1	 	:	8 7 8	1	1 1 1	! ! !	;	, , ,	!	:	1.94
50 ³	0.1	0.55	0.38	0.6	0.8	0.6	0.38	:	1 5 6	8 9 1	1	0.23
د _ر 0	1.3	2.0	2.57	3.2	2.7	3.6	3.16	3.65	0.27	1 1 1	0.06	0.05
- rio ₂	0.4	0.6	0.5	0.6	0.5	0.8	0.62	0.96	0.11	1	0.28	1 1 1
I												

GWKL: average of three Archean Knife Lake grayaverage Cenozoic-Mesozoic shale (Clarke, SH: average Paleozoic shale (Clarke, 1924) SS: average sandstone (Pettijohn, 1963) average graywacke (Pettijohn, 1963) SHAV: average shale (Clarke, 1924) wackes (Grout, 1933) SHCM: 1924) GW:

SHKL: average of three Archean Knife Lake shales (Grout, 1933)

pelagic red clay (El Wakeel and Riley, 1961) MONT: average of 8 montmorillonites (Grim, 1968) average of two saponites (Grim, 1968) PRC: SAP:

average of four nontronites (Grim, 1968) modern seawater (Turekian, 1969) : TNON SEA:

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AL203	1 8 8	50.00	;	 			1 1 1	5	1				rock, Mesat
HAL	1 1 1	: : :		0.0	0.66	52.0	! ! !	0.0	59.57	`0	0.0	8 1 1	taite 1
ANH	1 1 1	1	1 1 1	1 1 1	40.61	1 1 8	1.87	1 1 1	8 3 1	56.82	1 1 1	•	-minnesc
DOL	0.73	1 8 1	0.94	20.48	30.97	1 1 1	1	47.51	1 1 1		 	1 1 1	enalite
LS	5.19	0.81	0.38	7.9	42.61	0.05	0.77	41.58	0.02	0.27	0.33	0.06	ГАС: ğте
TAC	51.0	1.09	27.1	5.3	0.04	!	6.4	0.77	:	1	1		-
SID	46.5	0.24	18.9	3.1	1.9		1.15	19.96	1 1 1	0.27		1 8 8	dist-
MAG 3	22.7	0.31	33.5	3.9	4.5	1	1 1 1	21.3	8 9 1	1 1 1	, , ,	0.01	enominee
MAG2	45.7	Ò.28	30.0	2.7	1.04	8	1.54	8.0	8 9 9	1	1 1 1	8 8 1	ition, M
MAG1	34.4	0.9	38.5	2.3	1.7	1 1 1	0.44	7.6	0 5 0	0.02	0.13	0.02	ron forma
t HEM	40.1	0.8	36.3	2.0	1.4	1	1 1 1	2.6	:	0.02		8 1 1	matite i
Componen	sio,	A1,03	Fe .	MgO	Ca0	Na ₂ 0	- ч ² о	c_{0}^{2}	c1	so	K ₂ 0	Ti02	HEM: he

HEM: hematite iron formation, Menominee district (James, 1954)

MAG1: magnetite iron formation, Gogebic

district (Huber, 1959)

MAG2: magnetite-chert, Mesabi district (Gruner,1946) MAG3: magnetite-chert, Temiscamie (Quirke, 1961 and Quirke et al, 1960)

SID: carbonate iron formation, Gunflint district (Irving and Van Hise, 1892; Goodwin, 1956)

TAC: greenalite-minnesotaite rock, Mesabi district (Leith, 1903)

LS: average limestone (Clarke, 1924)

DOL: dolomite rock (Bayley, 1904)

ANH: anhydrite rock (Stewart, 1963, 22J; Clarke, 1915)

HAL: halite rock (Stewart, 1963, 24A)

AL203: hypothetical aluminum-rich rock

that the relative proportions of some of the metal ions in seawater may have changed through geologic time, and that its total salinity may have been different by a small factor. These differences would have been greater in the early Precambrian than in the Phanerozoic (Ronov, 1968; and Lafon and MacKenzie, 1971). The choice of an alternate to modern seawater as a final seawater composition in the mass balance calculations, however, would only slightly alter the results. The mass of the rockforming components in any reasonable estimate of seawater composition is small compared to their mass in the sediments. Use of an alternative composition for the final seawater to achieve a better balance would at best transfer observed discrepancies in the balance to a probable error in the estimate of the composition of the alternative. As the differences between the composition of modern seawater and estimates of earlier seawater compositions are approximately the same as the uncertainties in those estimates, it is preferable for the purposes of this study to use the known composition of modern seawater for the final seawater composition in the mass balance calculations. This choice prevents mass balance discrepancies from being hidden in the probable error in the estimate of the final seawater composition.

The component proportions of modern seawater are listed in Table 1.

Anorthositic crust.

The composition for the primordial crust is estimated from analyses of anorthosites that have been suggested to be remnants of a primordial anorthositic crust (Windley, 1970). The composition used in the mass balance is an average anorthosite composition in column D, Table 2.

Analyses of composite materials considered representative of the Lunar highlands (Lowman, 1976) are tabulated for comparison, as the analogy with the Lunar primordial crust is implicit in the anorthositic crustal model. The choice of ancient terrestrial anorthosites for the mass balance calculations rather than lunar materials is in recognition of the probable differences in the overall chemical compositions of the earth and the Moon.

Component	A	В	С	D	E	F	G
sio ₂	46.77	46.64	46.86	46.76	45.2	45.1	47.9
TiO ₂	0.33	0.15	0.03	0.17	1.0	0.6	1.7
A1203	27.43	25.53	33.05	28.67	21.7	26.7	17.6
Fe_20_3	1.59	0.70	0.46	0.92		0.0	0.0
FeO	3.17	4.41	0.48	2.69	7.9	5.5	10.4
MnO	0.03	0.05	0.01	0.03		0.1	0.1
MgO	2.86	6.81	0.42	3.36	9.7	5.9	9.2
CaO	14.74	13.84	16.53	15.04	13.1	15.4	11.2
Na ₂ 0	1.93	1.05	1.99	1.66	0.4	0.5	0.7
κ ₂ 0	0.25	0.00	0.04	0.10	0.2	0.1	0.6

Table 2. Compositions of anorthosites and Lunar crustal materials

A: homogenous hornblende anorthosite, southern West Greenland (Windley, 1969)

B: layered hyperstheme anorthosite, southern West Greenland (Windley, 1969)

C: anorthosite, Sittamundi complex, India (Subramanian, 1956)

D: average of A, B, and C

E: average composition of three massif (Lunar highland) derived categories of sample, Apollo 17 (Lowman, 1976)

F: average of six soils from several Apollo 16 stations (Lowman, 1976)
G: average of six Frau Mauro soils, taken as representative of Lunar highland compositions with respect to major elements (Lowman, 1976)

Primitive acid sea.

The composition of the primitive ocean is derived from a weathering model developed by Lafon and MacKenzie (1971) for the primordial earth under environmental conditions as suggested by Shaw, i. e. weathering a primordial crust by acid seas derived from the excess volatiles released by early differentiation of the cruat. Their estimate of excess volatiles is from the chemical mass balance work of Horn and Adams (1966).

Estimate of Mass of Excess Volatiles

 $H_{2}O = 16,700 \times 10^{20} \text{grams}$ C as CO₂ 1,100 x 10²⁰ grams S = 31 x 10²⁰ grams N = 39 x 10²⁰ grams Cl = 560 x 10²⁰ grams H, Br, B, As, F 16 x 10²⁰ grams (Lafon and MacKensie, 1971, after Horn and Adams, 1966)

By assuming the volatiles are entirely dissolved in the aqueous phase, and considering only the major reactive species, Lafon and Mac-Kenzie derived the following primitive acid sea, with a total mass of $18,460 \times 10^{20}$ grams:

Primitive A	Acid	Sea	
Dissolved Species		Concent (Moles/	tration /kg H ₂ 0)
H ₂ CO ₃		1.51	L
HC1		0.94	+6
н ₂ s		0.05	58
(Lafon and	Mack	Kenzie,	1971)

The assumption of total dissolution is not entirely accurate, but is justified for a balance carried to neutralization. CO_2 will continue to be dissolved at saturation levels until its mass is distributed between the sediments and the dissolved aqueous species, with atmospheric CO₂ levels approximating today's.

The initial pH of the model acid sea would be approximately zero, with H^+ contributed primarily by HCl, which dissociates completely at the estimated concentration. H_2CO_3 and H_2S do not significantly dissociate at this pH. They would remain in solution as uncharged species until the seas were neutralized to a pH of approximately 4. Their dissociation will maintain the pH at this level until neutralization reduces their total concentrations to approximately their present levels in seawater.

The total mass of the major reactive species is applied to the mass balance calculations. The mass of these volatiles in the atmosphere is insignificant compared to their mass in the hydrosphere and the sedimentary pile (Poldervaart, 1955), so that the calculations provide a good approximation of their distribution after neutralization of the primitive acid seas. With this application, the total acidity of the primitive sea is 2.57 equivalents per kilogram. This provides, for a primitive sea mass of 18,460 x 10^{20} grams, 47.5 x 10^{20} equivalents of acid to be neutralized by the primordial crust.

Proportions of primitive acid sea and primordial crust.

The minimum mass of anorthositic crust required to neutralize the primitive acid seas can be approximated if it is assumed that all of the metals in the rock react with the seas. The equation for calculating the neutralizing capacity per gram of crust, for each component oxide, is as tollows:

Number of equivalents of metal ion = (<u>Mass of oxide per gram crust</u>)(<u>Charge on ion</u>)(<u>Gravimetric factor</u>) Atomic weight of metal

For a crustal composition from column D, Table 2, the neutralizing capacity of the primordial crust is 0.057 equivalents per gram (Table 3, below).

Table 3. Calculation of maximum neutralizing capacity of anorthositic primordial crust, per gram of crust.

SiO₂ = .4676g = 0.03113 equiv. Si⁴⁺ TiO₂ = .0017g = 0.00009 equiv. Ti⁴⁺ Al₂O₃ = .2867g = 0.01687 equiv. Al³⁺ Fe₂O₃ = .0092g = 0.00035 equiv. Fe³⁺ FeO = .0269g = 0.00112 equiv. Fe³⁺ MgO = .0336g = 0.00168 equiv. Mg²⁺ CaO = .1504g = 0.00536 equiv. Ca²⁺ Na₂O = .0166g = 0.00054 equiv. Na⁺ K₂O = <u>.0010g</u> = <u>0.00002</u> equiv. K⁺ Total = 1.00g = 0.05714 equiv. metal ions

830 x 10^{20} grams of crust are thus required to neutralize the 47.5 x 10^{20} equivalents of acid in 18,460 x 10^{20} grams of primitive sea. This is a ratio of approximately 96 percent sea to 4 percent crust.

It is not realistic to assume such an extreme neutralizing capacity for the crust, as even at the low initial pH level, metals such as silicon and aluminum do not go into solution as ions. Only the more soluble metals can be expected to react to neutralize the acid, so that the amount of crust required for neutralization may be greater than the estimated 830 x 10^{20} grams by at least an order of magnitude.

Mass balance for each trial suite of sedimentary rock types is thus calculated for a range of primordial anorthositic crust : primitive acid sea mass ratios from 96 : 4 (770 x 10^{20} grams crust + 18,460 x 10^{20} grams sea) to 60 : 40 (12,310 x 10^{20} grams crust + 18,460 x 10^{20} grams sea). The results of the mass balance calculations, particularly the balance

of the volatiles, approximate the effective point of neutralization within this range. Component proportions for mixtures of primordial anorthositic crust and primitive acid sea are listed in Table 4.

Table 4. Component proportions of primordial anorthositic crust plus primitive acid sea mixtures used in chemical mass balance calculations.

Component	CR4	CR10	CR15	CR20	CR25	CR 30	CR 35	CR40
SiO ₂	1.87	4.68	7.02	9.36	11.70	14.04	16.38	18.72
A1203	1.15	2.87	4.31	5.74	7.18	8.61	10.05	11.48
Fe	0.11	0.27	0.41	0.54	0.68	0.81	0.95	1.08
MgO	0.14	J. 34	0.51	0.68	0.85	1.02	1.19	1.36
Ca0	0.60	1.50	2.25	3.00	<u>.</u> 3.75	4.50	5.25	6.00
Na ₂ 0	0.07	0.17	0.26	0.34	0.43	0.51	0.60	0.68
H ₂ 0	86.87	81.44	76.92	72.39	67.87	63.34	58.82	54.29
co ₂	6.38	5.99	5.65	5.32	4.99	4.66	4.32	3.99
C1	2.91	2.73	2.58	2.42	2.27	2.12	1.97	1.82
so3	0.40	0.38	0.36	0.34	0.32	0.29	0.27	0.25
κ ₂ 0	0.004	0.01	0.015	0.02	0.025	0.03	0.035	0.04
TiO ₂	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08

CR4:	4% crust (770 x 10^{20} g crust + 18460 x 10^{20} g sea)
CR10:	10% crust	$(2050 \times 10^{20} \text{g crust} + 18460 \times 10^{20} \text{g sea})$
CR15:	15% crust	$(3260 \times 10^{20} \text{g crust} + 18460 \times 10^{20} \text{g sea})$
CR20:	20% crust	$(4620 \times 10^{20} \text{g crust} + 18460 \times 10^{20} \text{g sea})$
CR25:	25% crust	$(6150 \times 10^{20} \text{g crust} + 18460 \times 10^{20} \text{g sea})$
CR 30:	30% crust	$(7910 \times 10^{20} \text{g crust} + 18460 \times 10^{20} \text{g sea})$
CR35:	35% crust	$(9940 \times 10^{20} \text{g} \text{ rust} + 18460 \times 10^{20} \text{g} \text{ sea})$
CR40:	40% crust	$(12310 \times 10^{20} \text{g crust} + 18460 \times 10^{20} \text{g sea})$

RESULTS OF CALCULATIONS

The first objective of the mass balance calculations was to find a suite of sedimentary rock types that satisfied the mass balance equation:

Primordial crust + Primitive acid sea = b_1 Sediment₁ +

 b_2 Sediment₂ + . . . + b_k seawater

such that the residuals of the component oxides were reasonably small and the b coefficients for the sedimentary rock types were positive within normal error (one standard deviation), so that the equation balanced well with all of the sediment types on the products side of the equation. A value of 2.0 or less for the sums of squares of residuals (SSR) was taken as a preliminary indicator of a good balance. An examination of individual component residuals, however, is necessary in the interpretation of the significance of the results of the regressions.

The second stage was to improve the balance by trying alternative sediments of similar types, ideally including Archean sedimentary rock compositions in the suites. The ultimate goal was to find a suite of sedimentary rock types that might be reasonably compared to observed suites of early Archean sediments and metasediments.

Of forty-seven calculated suites, six approximated a reasonable chemical mass balance with the modeled primordial anorhtositic crust. These balanced at primordial crust to primitive acid sea mass proportions of approximately 30 : 70.

No suites balanced that included a sandstone or a graywacke, as there is insufficient SiO_2 in the anorthositic weathering parent, with respect to Al_2O_3 , for a sandstone to balance on the products side of the equation. Suites containing clays or shales, and no sandstones, balanced

only if the suite also contained a hypothetical aluminum-rich rock. The anorthositic weathering parent has an excess of alumina with respect to the other components, when compared to clays and shales, so that an aluminum-rich rock must be included as a product if the equation is to balance.

The results of the calculations for the six sedimentary suites that approximated a reasonable chemical mass balance are listed in Tables 5 through 10, below.

When the proportions of the sedimentary rock types for the six tabulated calculations are recalculated excluding seawater, and averaged, the composite sedimentary suite looks something like this:

Shale, or clay,		
representing mudstones:		55%
Carbonate-rich iron		
formation:	1	to 2%
Limestone:		2 3%
Evaporites:	1	to 2%
Aluminum-rich rock:		20%

The suite is additionally characterized as being low in sodium and quite low in potassium, as the available mass of these components in the anorthositic crust is insufficient to meet the requirements for them in the estimated sedimentary suite.

Table 5. Results of sedimentary chemical mass balance calculation (potassium and titanium excluded from calculation).

			Variable	Standard
Rock Type			Coefficient	Deviation
Paleozoic shal	.e		0.2287	0.0136
Gogebic magnet	ite iron for	mation	-0.0095	0.0156
Limestone			0.1165	0.0307
Dolomite			-0.0258	0.0305
Seawater			0.6326	0.0056
Aluminum-rich	rock		0.0955	0.0118
Component	Y. Est.	Y. Obs.	Residual	% Residual
SiO ₂	14.03	14.04	-0.0124	-0.09
A1203	8.61	8.61	0.0000	0.00
Fe	0.82	0.81	0.0119	1.47
MgO	1.03	1.02	0.0089	0.87
CaO	4.51	4.50	0.0080	0.18
Na ₂ 0	1.16	0.51	0.6482	127.10
H ₂ O	63.35	63.34	0.0079	0.01
co ₂	4.65	4.66	-0.0091	-0.20
C1	1.23	2.12	-0.8904	-42.00
so ₃	0.31	0.29	0.0240	8.28

SSR = 1.2140

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30% crust, 70% sea

Table 6. Results of sedimentary chemical mass balance calculation (potassium and titanium excluded from calculation)

			Variable	Standard
Rock Type			Coefficient	Deviation
Paleozoic shal	e		0.2272	0.0120
Temiscamie mag	netite iron	formation	-0.0103	0.0173
Limestone			0.1154	0.0173
Dolomite			-0.0223	0.0318
Seawater			0.6327	0.0056
Aluminum-rich	rock		0.0959	0.0117
Component	Y. Est.	Y. Obs.	Residual	% Residual
510 ₂	14.03	14.04	-0.0130	-0.09
A1203	8.61	8.61	0.0000	0.00
Fe	0.84	0.81	0.0267	3.30
MgO	1.07	1.02	0.0499	4.89
Ca0	4.54	4.50	0.0351	0.78
Na ₂ 0	1.16	0.51	0.6467	126.80
H ₂ 0	63.35	63.34	0.0078	0.01
co ₂	4.62	4.66	-0.0448	-0.96
C1	1.23	2.12	-0.8903	-42.00
so ₃	0.31	0.29	0.0230	7.93

SSR = 1.2181

30% crust, 70% sea

Table 7. Results of sedimentary chemical mass balance calculation (potassium and titanium excluded from calculation)

			Variable	Standard
Rock Type			Coefficient	Deviation
Cenozoic-Mesozoic shale			0.2476	0.0151
Temiscamie magnetite iron formation			-0.0057	0.0198
Limestone			0.0817	0.0362
Dolomite			-0.0116	0.0369
Seawater			0.6297	0.0065
Aluminum-rich rock			0.1026	0.0133
Component	Y. Est.	Y. Obs.	Residual	% Residual
sio ₂	14.00	14.04	-0.0374	-0.27
A1203	8.61	8.61	0.0000	0.00
Fe	0.90	0.81	0.0850	10.49
MgO	1.19	1.02	0.1655	16.23
CaO	4.62	4.50	0.1172	2.60
Na ₂ 0	1.37	0.51	0.8590	168.43
H ₂ O	63.34	63.34	0.0044	0.01
co ₂	4.51	4.66	-0.1489	-3.20
c1	1.22	2.12	-0.8968	-42.30
so3	0.36	0.29	0.0749	25.83

SSR = 1.6198

30% crust, 70% sea

Table 8. Results of sedimentary chemical mass balance calculation.

			Variable	Standard	
Rock Type			Coefficient	Deviation	
Paleozoic shal	e		0.2257	0.0216	
Temiscamie magnetite iron formation			-0.0090	0.0146	
Limestone			0.1167	0.0433	
Dolomite			-0.0236	0.0421	
Halite			0.0031	0.0087	
An h ydrit e			-0.0008	0.0117	
Seawater			0.6327	0.0071	
Aluminum-rich	rock		0.0963	0.0146	
Component	Y. Est.	Y. Obs.	Residual	% Residual	
SiO2	13.97	14.04	-0.0705	-0.50	
A1 ₂ 0 ₃	8.61	8.61	0.0000	0.00	
Fe	0.87	0.81	0.0605	7.47	
MgO	1.06	1.02	0.0355	3.48	
CaO	4.53	4.50	0.0253	0.56	
Na ₂ 0	1.32	0.51	0.8067	158.18	
H ₂ O	63.34	63.34	0.0015	0.00	
co ₂	4.63	4.66	-0.0319	-0.68	
C1	1.41	2.12	-0.7055	-33.28	
so ₃	0.27	0.29	-0.0181	-6.24	
к ₂ 0	0.88	0.03	0.8527	2842.33	
Tio ₂	0.19	0.06	0.1275	212.50	

SSR = 1.9037 30% crust, 70% sea Table 9. Results of sedimentary chemical mass balance calculation.

	Variable	Standard
Rock Type	Coefficient	Deviation
Montmorillonite	0.3038	0.0133
Temiscamie magnetite iron formation	0.0068	0.0167
Limestone	0.1009	0.0120
Halite	0.0056	0.0073
Anhydrite	0.0043	0.0092
Seawater	0.5368	0.0064
Aluminum-rich rock	0.0805	0.0167

Component	Y. Est.	Y. Obs.	Residual	% Residual
sio ₂	16.32	16.38	-0.0646	-0.39
A1203	10.05	10.05	0.0000	0.00
Fe	0.90	0.95	-0.0502	-5.28
MgO	2.07	1.19	0.8797	73.92
Ca0	5.07	5.25	-0.1814	-3.46
Na ₂ 0	1.28	0.60	0.6795	113.25
H ₂ O	58.82	58.82	-0.0005	0.00
co ₂	4.35	4.32	0.0251	0.58
C1	1.38	1.97	-0.5945	-30.18
so3	0.40	0.27	0.1296	48.00
к ₂ 0	0.14	0.04	0.1074	268.50
TiO ₂	0.04	0.07	-0.0305	-43.57

SSR = 1.6586 35% crust, 65% sea Table 10. Results of sedimentary chemical mass balance calculation.

	Variable	Standard
Rock Type	Coefficient	Deviation
Montmorillonite	0.2956	0.0262
Carbonate iron formation	0.0126	0.0269
Limestone	0.0997	0.0130
Halite	0.0056	0.0072
Anhydrite	0.0049	0.0094
Seawater	0.5383	0.0077
Aluminum-rich rock	0.0837	0.0154

Component	Y. Est.	Y. Obs.	Residual	% Residual
SiO ₂	16.32	16.38	-0.0606	-0.37
A1203	10.50	10.50	0.0000	0.00
Fe	0.89	0.95	-0.0556	-5.05
MgO	2.04	1.19	0.8523	71.62
Ca0	5.02	5.25	-0.2318	-4.42
Na ₂ 0	1.28	0.60	0.6762	112.70
н ₂ 0	58.82	58.82	-0.0005	0.00
co ₂	4.40	4.32	0.0814	1.88
C1	1.38	1.97	-0.5916	-30.03
so3	0.44	0.27	0.1657	61.37
к ₂ 0	0.14	0.04	0.1048	262.00
TiO ₂	0.04	0.07	-0.0315	-45.00

SSR = 1.6402

35% crust, 65% sea (Best volatile balance at 32% crust)

The approximate mass of these sediments can be calculated from the masses of the starting materials. The mass of the primitive acid sea is fixed at 18,460 x 10^{20} grams by the estimate of excess volatiles. The necessary amount of anorthositic crust for neutralization is added to the system to obtain the appropriate crust to sea mass ratio, providing a fixed total mass for a given mixture of primordial crust and primitive acid sea. By subtracting the derived proportion of final seawater from the total mass for each of the six tabulated calculations above, the mass of the derived sediments can be obtained. The mean for the six tabulated sedimentary suites is $10,850 \times 10^{20}$ grams. This value is 30% to 70% less than estimates of the total mass of sediments and sedimentary rocks (Garrels and MacKenzie, 1971; Garrels et al, 1972; Horn and Adams, 1966; and Li, 1972). The calculated mass of the final neutralized sea is 16.200 x 10^{20} grams, which is within the range of values of estimates of the total mass of the hydrosphere (Mason, 1966; Poldervaart, 1955; Ronov, 1968; and Garrels and MacKenzie, 1971).

EFFECTS OF SEDIMENTARY RECYCLING

The amount of the $10,850 \times 10^{20}$ grams of sediment derived from the weathering of a primordial anorthositic crust that may remain at the present may be estimated with the aid of sedimentary recycling models. The timetable for Shaw's crustal evolution model places the deposition of these sediments in a period between 3900 million years before present and the beginning of the development of greenstone belts, which date to approximately 3500 million years before present. Sedimentary recycling processes thus will have been operating on these primitive sediments for a mean of 3700 million years.

Estimates of the total mass of sediments and sedimentary rocks range from 14,000 x 10^{20} grams to 32,000 x 10^{20} grams. The most frequently derived estimates are on the order of 24,000 x 10^{20} grams. This intermediate figure is used for estimates of the proportion of the total sedimentary mass represented by the surviving portion of the primitive sediments derived from the weathering of a primordial crust.

Estimates of sedimentary recycling rates vary. Rates from the recycling models of Garrels et al (1972) and Blatt and Jones (1975) provide upper and lower limits, respectively, for the expected preservation of the derived sedimentary suite.

Blatt and Jones estimate a sediment half-age of 130 million years from data on the areal extent of exposures of Paleozoic and younger sedimentary rocks. This rate provides a survival fraction of 2.7 x 10^{-9} for sediments 3700 million years old, or 2.9 x 10^{15} grams preserved from the derived mass of of 10,850 x 10^{20} grams. This is a fraction of 1.2 x 10^{-9} of the present sedimentary mass, a little more than one millionth. If the Blatt and Jones recycling rate is thus extrapolated 3700 million years into the past, the probability of finding a sedimentary rock of this age would be remote.

Garrels et al have estimated different recycling rates for different sedimentary rock types. This reflects differences in resistance to erosion due to differences in solubility. Their recycling rates are based on maximum thickness data for sedimentary rocks, including data on exposures of Precambrian sediments and metasediments.

This model assigns a half-age of 600 million years for sandstones and shales; the survival fraction for 3700 million year old rocks is 0.01. The sandstone and shale recycling rate is assumed to also apply

to ironstones. Carbonates are assigned a half-age of 300 million years, for a 3700 million year survival fraction of 1.9 x 10^{-4} . Evaporites are assigned a half-age of 200 million years, for a 3700 million year survival fraction of 2.7 x 10^{-6} .

These survival fractions leave 59.7 x 10^{20} grams of shale, 1.63 x 10^{20} grams of iron formation, 0.474 x 10^{20} grams of limestone and 4.4 x 10^{16} grams of evaporite from the 10,850 x 10^{20} grams of sediment derived from the primordial crust. As aluminum oxides are less soluble than silica, it is reasonable to assume the sandstone and shale recycling rate would apply to the aluminum-rich rock, so the amount preserved would be 21.7 x 10^{20} grams. The total amount of sediment preserved would be 83.5 x 10^{20} grams, a fraction of 7.7 x 10^{-3} of the total sedimentary mass, approximately one one-hundred-thirtieth. This fraction suggests the probability of locating a remnant of sedimentary rock of this age is quite good.

The differential recycling model of Garrels et al has an important effect on the proportions of rock types after recycling processes have acted for 3700 million years. After differential recycling for this length of time at the recycling rates above, the sedimentary suite derived from a primordial anorthositic crust looks like this:

Shale, or clay,	
representing mudstones:	71.5%
Carbonate-rich	
iron formation:	2.0%
Limestone:	0.6%
Evaporites:	Nil
Aluminum-rich rock	26.0%

As an aluminum-rich rock would be as persistant as a shale, if the primordial crust were anorthositic we could expect to find, in ancient sedimentary rocks, a mass of aluminum-rich rock of approximately onethird the mass of shales of the same age. This trend should continue in sedimentary rocks of younger age age until enough silica is added to the sedimentary system from the erosion of younger, more siliceous igneous rocks for the aluminum-rich rocks to be changed to clays and aluminosilicates by weathering and resedimentation, or by metamorphism. Within the framework of Shaw's model of crustal evolution, these changes could begin with the onset of greenstone belt activity; with the addition of sedimentary material derived from the weathering of new igneous rocks, the chemical character of the sedimentary mass would begin to change, and increasingly younger sedimentary rocks would look less like the material derived from the weathering of an anorthosite.

DISCUSSION OF RESULTS OF CALCULATIONS

The six tabulated estimates of the proportions of sedimentary rock types calculated from the mass balance equation provide an approximation of the proportions of sediment types that might result from the weathering of an anorthositic primordial crust by acid seas condensed from the earth's excess volatiles. The approximation does not resemble estimates of the proportions of sedimentary rock types presently in the crust.

The most apparent difference between the derived sedimentary suite and common sedimentary rocks is the high ratio of alumina to silica in the suite derived from the anorthosite. An anorthositic crust is so poor in silica with respect to alumina that a sandstone cannot be derived from it with a mass balance calculation. In order to balance the equation

with a clay or shale as a product, an aluminum-rich rock must be included in the product sedimentary suite; the anorthosite is silica deficient in comparison to clays and shales. Of common sedimentary minerals, only kaolinite minerals and aluminum hydroxides are sufficiently rich in aluminum to balance with the anorthosite.

In order to analyse the magnitude of this and other mass balance discrepancies, a limited number of calculations were made with other igneous rock types (granodiorite, andesite, and tholeiitic basalt from Hyndman, 1972) as the primordial crust. These were balanced against a sedimentary suite resembling the ones that balanced best with the anorthosite. No attempt was made to find the sedimentary suites that balanced best with these alternative crustal materials, as the purpose in their calculation was to aid in the evaluation of residual imbalances that occurred in calculations made for the anorthositic crust. The data for these calculations is listed in Tables 11 through 13, and the results of the calculations are in Tables 14 through 16, below.

These additional calculations showed that a material as rich in silica as a granodiorite is needed as a weathering parent if the crustal material is to balance with a sedimentary suite containing a quartz sandstone. Balances calculated with andesite and tholeiitic basalt as primordial crust produced positive coefficients for aluminum-rich rock in suites containing a shale and no sandstone. The aluminum excess in these materials, however, is not as great as that in the anorthosite.

The second major residual balance discrepancy is in potassium. Estimates using shales as the mudstones in the sedimentary suites showed a potassium deficiency on the order of 3000% of the amount available in

the anorthositic weathering parent. Estimates using low-potassium clays to represent mudstones showed potassium deficiencies on the order of 300%.

The andesite and tholeiitic basalt alternatives showed potassium deficiencies an order of magnitude smaller; these materials might balance well with low-potassium clays. The granodiorite alternative produced potassium residuals small enough to suggest that it would balance well with respect to potassium when balanced against a suite containing a shale and a sandstone, i. e. a suite more appropriate to its composition. These results indicate that the potassium balance discrepancy is not a result of the approach to the problem, it is rather the result of a real and serious potassium deficiency in the anorthositic weathering parent.

A third residual imbalance occurs with respect to sodium, and it is consistently related to an imbalance with respect to chlorine. The sodium residuals indicate a deficiency of approximately 100% to 150% of the amount of sodium available in the anorthosite. There is a consistent chlorine surplus of approximately 30% to 40% of the amount of chlorine in the model primitive acid sea.

Two factors may be working together to produce these balance discrepancies. The anorthositic weathering parent is certainly deficient in sodium compared to the proportions of this element in sedimentary rocks. Also, the estimate of the amount of chlorine in the earth's excess volatiles may be slightly high, as noted by Lafon and MacKenzie (1971). In the balance of the components, chlorine occurs on the products side of the equation in significant amounts only in seawater and halite; both of these require sodium in an approximate 3 : 4 mass ratio to the amount of chlorine. The amount of seawater estimated is mostly determined by the

H₂O mass, and the mass of chlorine not balanced in seawater must be balanced, accompanied by sodium, in halite rock. A sodium deficiency in the anorthositic weathering parent will restrict the amount of halite estimated, leaving a high negative value for the chlorine residual, which appears as a surplus in the primitive acid sea. Conversely, an actual chlorine surplus, resulting from a high value for the mass of chlorine in Horn and Adams' estimate of crustal mass balance, will accentuate any sodium deficiency by producing greater amounts of halite in the mass balance calculations.

Trends of residuals with increasing proportions of primordial crust to primitive acid sea demonstrate this reciprocal relationship. With an increasing proportion of crust, absolute values of the chlorine and sodium residuals converge toward zero. The other volatiles, H_2O , CO_2 , and SO_3 , have near zero residuals at a common ratio of primordial crust to acid sea, a ratio at which the values of the residuals for iron, magnesium, calcium, silica and aluminum also converge at zero. This proportion is in the range 30% to 35% crust for all of the good balances. The convergence of sodium and chlorine residuals, however, is at much higher crust to sea ratios.

The resolution of this imbalance is complicated by the uncertainty as to the composition of the seas in the early Precambrian. If, as Ronov (1968) suggests, the early oceans had higher Mg^{2+} : Na⁺ and Ca²⁺: Na⁺ ratios than modern seawater, the chlorine in the early neutralized oceans may have been electrically balanced by these ions, and these would be replaced by Na⁺ as it was introduced by the weathering of later igneous rocks. As noted in the discussion of the choice of a final seawater for these mass balance calculations, there is enough uncertainty as to the early

composition of seawater to preclude the choice of some alternative to modern seawater as the final seawater composition.

The mass balance calculations using alternative primordial crustal compositions were made primarily to evaluate this sodium-chlorine imbalance. Granodiorite and andesite, which contain approximately five times as much sodium as the anorthositic crust, balanced with much smaller chlorine and sodium residuals. This confirms that much of the imbalance is due to a sodium deficiency in the anorthosite. The chlorine balance, however, with these materials still requires a greater proportion of crust to sea than required for the balance of the other volatiles and the major metal oxides, suggesting that the sodium deficiency is accentuated by a high estimate of chlorine in the excess volatiles.

The calculations reported in Tables 7, 9 and 10 suggest imbalances of SO_3 . These apparent imbalances result from the method of reporting data. The best balances for these three calculations occurred at crust to sea proportions intermediate to ratios for which balances were actually calculated and results tabulated. The SO_3 residuals diverged far enough at the nearest data point to the best balance point to compute as high percentages of the small mass of SO_3 in the system. Graphs of residual values plotted against crust to sea proportions for all computed balances demonstrate that linear interpolation of residual values between calculated data points is justified. Such interpolation of values of SO_3 residuals for these three suites indicates that the SO_3 residuals converge to zero at the same crust to sea mass ratio the other well balanced components converge to zero.

The titanium imbalances indicated do not appear to be the result of an interpolation difficulty. These imbalances are consistent over the

full range of crust to sea ratios for the balance calculations in which they occur. Their geological significance is questionable, because the titanium proportions in all of the rock types are quite small, and they contribute little to the least squares estimate of mass balance. The titanium residuals have both positive and negative values, indicating titanium deficiencies and surpluses, respectively, for balances with quite similar sedimentary suites.

Component	GD4	GD10	GD15	GD20	GD25	GD30	GD35	GD40
510 ₂	2.68	6.69	10.03	13.38	16.72	20.06	23.41	26.75
A1203	0.63	1.57	2.35	3.13	3.92	4.70	5.48	6.26
Fe	0.12	0.29	0.44	0.59	0.74	0.88	1.03	1.18
MgO	0.06	0.16	0.24	0.31	0.39	0.47	0.55	0.60
Ca0	0.14	0.36	0.53	0.71	0.89	1.07	1.25	1.42
Na ₂ 0	0.15	0.38	0.58	0.77	0.96	1.15	1.34	1.54
H ₂ O	86.90	81.51	77.01	72.52	68.03	63.54	59.05	54.55
co ₂	6.38	5.99	5.65	5.32	4.99	4.66	4.32	3.99
C1	2.91	2.73	2.58	2.42	2.27	2.12	1.97	1.82
so3	0.40	0.38	0.36	0.34	0.32	0.29	0.27	0.25
K ₂ 0	0.12	0.31	0.46	0.61	0.77	0.92	1.07	1.23
TiO ₂	0.02	0.06	0.09	0.11	0.14	0.17	0.20	0.23

Table 11. Component proportions of granodiorite plus primitive acid sea mixtures used in analytical sedimentary chemical mass balance calculations.

GD4:	4% granodiorite, 96% sea
GD10:	10% granodiorite, 90% sea
GD15:	15% granodiorite, 85% sea
GD20:	20% granodiorite, 80% sea
GD25:	25% g ran odiorite, 75% sea
GD30:	30% granodiorite, 70% sea
GD35:	35% granodiorite, 65% sea
GD40:	40% granodiorite, 60% sea

Component	AD4	AD10	AD15	AD20	AD25	AD30	AD35	AD40
SiO ₂	2.17	5.42	8.13	10.84	13.55	16.26	18.97	21.68
A1203	0.69	1.72	2.58	3.43	4.29	5.15	6.01	6.87
Fe	0.27	0.67	1.01	1.34	1.68	2.01	2.35	2.68
MgO	0.17	0.44	0.65	0.87	1.09	1.31	1.53	1.74
Ca0	0.32	0.79	1.19	1.58	1.98	2.38	2.77	3.17
Na ₂ 0	0.15	0.37	0.55	0.73	0.92	1.10	1.28	1.47
H ₂ 0	86.90	81.53	77.05	72.56	68.08	63.60	59.12	54.64
co ₂	6.38	5.99	5.65	5.32	4.99	4.66	4.32	3.99
C1	2.91	2.73	2.58	2.42	2.27	2.12	1.97	1.82
so ₃	0.40	0.38	0.36	0.34	0.32	0.29	0.27	0.25
κ ₂ 0	0.04	0.11	0.17	0.22	0.28	0.33	0.39	0.44
T ¹⁰ 2	0.05	0.13	0.20	0.26	0.33	0.39	0.46	0.52

Table 12. Component proportions of andesite plus primitive acid sea mixtures used in analytical sedimentary chemical mass balance calculations.

AD4:	4% andesite, 96% sea
AD10:	10% andesite, 90% sea
AD15:	15% andesite, 85% sea
AD20:	20% andesite, 80% sea
AD25:	25% andesite, 75% sea
AD30:	30% andesite, 70% sea
AD35:	35% an desi te, 65% sea
AD40:	40% andesite, 60% sea

Component	TB4	TB10	TB15	TB20	TB25	TB 30	TB35	ТВ40
SiÓ ₂	2.03	5.08	7.62	10.17	12.71	15.25	17.79	20.33
A1203	0.56	1.41	2.11	2.81	3.52	4.22	4.92	5.63
Fe	0.36	0.91	1.36	1.81	2.27	2.72	3.17	3.62
MgO	0.25	0.63	0.95	1.27	1.59	1.90	2.22	2.54
CaO	0.42	1.04	1.56	2.08	2.61	3.13	3.65	4.17
Na 20	0.09	0.22	0.33	0.45	0.56	0.67	0.78	0.89
H ₂ O	86.91	81.53	77.05	72.57	68.10	63.62	59.14	54.66
co ₂	6.38	5.99	5.65	5.32	4.99	4.66	4.32	3.99
C1	2.91	2.73	2.58	2.42	2.27	2.12	1.97	1.82
so3	0.40	0.38	0.36	0.34	0.32	0.29	0.27	0.25
κ ₂ 0	0.03	0.08	0.12	0.16	0.21	0.25	0.29	0.33
TiO ₂	0.08	0.20	0.30	0.41	0.51	0.61	0.81	0.91

Table 13. Component proportions of tholeiitic basalt plus primitive acid sea mixtures used in analytical sedimentary chemical mass balance calculations.

TB4:	4% basalt, 96% sea
TB10:	10% basalt, 90% sea
TB15:	15% basalt, 85% sea
TB20:	20% basalt, 80% sea
TB25:	25% basalt, 75% sea
TB 30:	30% basalt, 70% sea
TB35:	35% basalt, 65% sea
TB40:	40% basalt, 60% sea

Table 14. Results of sedimentary chemical mass balance calculation, granodiorite crust.

		N	Standard		
Rock Type		Coefficient		Deviation	
Paleozoic sha	le	0.4389		0.0118	
Limestone			0.0452	0.0431	
Dolomite			-0.0121	0.0407	
Halite			0.0101	0.0087	
Anhydrite			-0.0084	0.0116	
Seawater			0.5338	0.0070	
Aluminum-rich rock			-0.0195	0.0143	
Component	Y. Est.	Y. Obs.	Residual	% Residual	
SiO2	26.65	26.75	-0.1034	-0.39	
A1203	6.26	6.26	0.0000	0.00	
Fe	2.24	1.18	1.0641	90.18	
MgO	1.23	0.63	0.6022	95.59	
Ca0	1.87	1.42	0.4463	31.43	
Na ₂ 0	1.75	1.54	0.2069	13.44	
н ₂ о	54.55	54.55	-0.0005	0.00	
co ₂	3.42	3.99	-0.5700	-14.29	
C1	1.64	1.82	-0.1811	-9.95	
so3	-0.07	0.25	-0.3190	-127.60	
к ₂ о	1.62	1.23	0.3920	31.87	
TiO2	0.35	0.23	0.1238	53.83	

SSR = 2.3761 40% granodiorite, 60% sea Table 15. Results of sedimentary chemical mass balance calculation, andesite crust.

		7	Variable	Standard
Rock Type		Coefficient		Deviation
Paleozoic shale		0.3117		0.0090
Limestone			0.0331	
Dolomite			0.0312	
Halite		0.0088		0.0067
Anhydrite		-0.0017		0.0089
Seawater			0.0054	
Aluminum-rich rock		0.0173		0.0110
Component	Y. Est.	Y. Obs.	Residual	% Residual
SiO,	18.98	18.97	0.0115	0.06
A1,0,	6.01	6.01	0.0000	0.00
Fe	1.63	2.35	-0.7227	-30.75

10	1.05	2.55	0.7227	50.75
MgO	1.64	1.53	0.1150	7.52
CaO	2.80	2.77	0.0343	1.24
Na ₂ 0	1.63	1.28	0.3493	27.29
H ₂ O	59.12	59.12	0.0002	0.00
co ₂	4.26	4.32	-0.0578	-1.34
C1	1.66	1.97	-0.3058	-15.52
so3	0.25	0.27	-0.0245	-9.07
κ ₂ ο	1.16	0.39	0.7745	198.59
TiO ₂	0.25	0.46	-0.2083	-45.28

SSR = 1.3995 35% andesite, 65% sea Table 16. Results of sedimentary chemical mass balance calculation, tholeiitic basalt crust.

		7	/ariable	Standard	
Rock Type		(Coefficient	Deviation	
Paleozoic sha	le		0.2515	0.0143	
Limestone			0.0267	0.0523	
Dolomite			0.0500	0.0494	
Halite			0.0042	0.0106	
Anhydrite			0.0002	0.0141	
Seawater			0.6350	0.0085	
Aluminum rich	rock		0.0015	0.0173	
Component	Y. Est.	Y. Obs.	Residual	% Residual	

				,,
SiO ₂	15.31	15.25	0.0647	0.42
A1203	4.22	4.22	0.0000	0.00
Fe	1.34	2.72	-1.3803	-50.75
MgO	1.95	1.90	0.0456	2.40
CaO	3.09	3.13	-0.0443	-1.42
^{Na} 2 ^O	1.40	0.67	0.7287	108.76
H ₂ O	63.62	63.62	0.0013	0.00
co ₂	4.70	4.66	0.0355	0.76
C1	1.48	2.12	-0.6372	-30.06
so ₃	0.32	0.29	0.0316	10.90
κ ₂ 0	0.95	0.25	0.6961	278.44
TiO ₂	0.20	0.61	-0.4072	-66.75

SSR = 3.5031 30% tholeiitic basalt, 70% sea COMPARISON OF SEDIMENT DERIVED FROM PRIMORDIAL ANORTHOSITIC CRUST BY MASS BALANCE WITH ANCIENT SEDIMENTARY ROCKS

The oldest known terrestrial rocks are the metasedimentary Isua supracrustals of southern West Greenland. Iron formation from this succession has been dated at $3760 \stackrel{+}{.} 70$ million years (Moorbath et al, 1973). This date has been interpreted as the age of metamorphism of the iron formation, and the geochronologists suggest the depositional age may be as great as 3900 million years.

The Isua supracrustals have been interpreted as a shallow-water shelf facies (Bridgwater et al, 1973), with elongate masses of ultrabasic rocks between sedimentary successions suggestive of submarine lavas (Bridgwater and McGregor, 1974). The bulk of the succession consists of carbonate-rich quartzofeldspathic metasediments, quartzite-magnetite and siderite-magnetite iron formation, carbonate-bearing quartzites, and silicarich carbonate-bearing garnet-biotite-muscovite schists. Conglomeratic units contain boulders, cobbles and pebbles of muscovite-rich quartzofeldspathic rocks, for which preliminary analyses show high-potassium granitic compositions, in a fine-grained carbonate-rich matrix; and units of quartzite pebbles in garnet-biotite-muscovite schists (Bridgwater and McGregor, 1974; and Allaart, 1975).

The Isua metasediments compare favorably to the sedimentary suite derived from the mass balance calculations only with respect to the dominance of pelitic rocks (shales and clays, or schists), and the presence of significant amounts of iron formation. Closer comparison only emphasizes the differences.

The schist mineralogies in the Isua supracrustals indicate a high potassium content, and these could not be derived from the weathering of

the modeled primordial anorthositic crust. This discrepancy is emphasized by the presence of potassium-rich granitic cobbles and boulders in Isua conglomerates; these suggest derivation from the weathering of a granitic crust rather than one of anorthositic composition.

The Isua sediments are remarkably silica rich. The schists are quartz-bearing, and the ironstones are notably quartz rich. Quartzites are volumetrically significant in the succession. The modeled anorthositic crust is quartz deficient with respect to shales, and cannot be expected to produce quartz sandstones. There is no evidence in the Isua succession of an aluminum-rich rock that would be volumetrically significant in a sedimentary suite derived from the weathering of a primordial anorthositic crust.

The preliminary mapping teams who have examined the Isua sediments suggest that they are a shallow-water continental shelf facies, which is reasonably interpretable as deposition in a shallow intracontinental sea. The tectonic setting, as well as age, of the succession is thus appropriate for sediments weathered from the primordial crust. The succession does not lithologically resemble the suite predicted by chemical mass balance calculations for the weathering of an anorthositic primordial crust. A granitic composition is more strongly indicated for the primordial crust.

The other known rocks of sedimentary origin sufficiently old to represent the weathering products of a primordial crust are the sediments in the 3300 to 3400 million year old Swaziland Sequence of South Africa (Hurley et al, 1972; and Allsopp et al, 1968 and 1974). The characteristic associations of these oldest sediments on the African craton indicate that their origin is related to the development of green-

stone belts, and they cannot be compared to the sedimentary products predicted by a mass balance calculation for the weathering of the first crust.

EFFECTS OF A PRIMORDIAL ANORTHOSITIC CRUST ON SEDIMENTARY ROCK COMPO-SITIONS THROUGH GEOLOGIC TIME.

Sedimentary recycling rates predict that a maximum of one percent of the material derived from the weathering of a primordial crust would be preserved as first cycle sedimentary rocks. The other 99 percent will be recycled to become part of younger sediments, and a distinctive anorthositic composition may be expected to impart a chemical imprint to the sedimentary mass. This imprint will be stronger the closer in age subsequent cycles of sedimentation are to the first cycle, and the waning of this chemical imprint should appear as marked trends in the chemistry of sedimentary rocks through geologic time.

These expected chemical trends can be approximated by comparing the composition of the original anorthositic material to the composition of the average Precambrian sediment, and calculating the mass and composition of the new igneous material that must be added to achieve the observed average chemistry.

The equation for this calculation is, for each component:

(1-X)(proportion of component in anorthositic crust) +

(X)(proportion of component in rock to be added) =

proportion of component in average Precambrian sediment.

The composition of the average Precambrian sediment used in this calculation is the estimate by Reilly and Shaw (1967) for the sediments of the Canadian shield. Results of the calculations for values of X from 0.5 to

0.8, representing ratios of primitive sediment to new sedimentary material of 1 : 1 to 1 : 4, are tabulated below:

Table 17. Estimate of mass and composition of new igneous material that must be added to anorthosite-derived sediments to achieve average Precambrian sedimentary composition.

Component	Proportion in anorthosite	Proportion in average Precambrian sediment	Proportion in material to be added to achieve average Precambrian composition for indicated value of X			
			0.50	0.6/	0.75	0.80
sio ₂	47.5	66.5	85.5	76.0	72.8	71.3
A1203	29.1	15.3	1.5	8.4	10.7	11.9
Fe	2.8	5.6	8.4	7.0	6.5	6.3
MgO	3.4	3.0	2.6	2.8	2.9	2.9
Ca0	15.3	4.9	-5.5	-0.3	1.4	2.3
Na ₂ 0	1.7	3.1	4.5	3.8	3.6	3.5
к,0	0.1	1.7	3.3	2.5	2.2	2.1
TIO2	0.2	0.6	1.0	0.8	0.7	0.7

The composition of the average Precambrian sediment can be achieved if the sedimentary material derived from the primordial anorthositic crust is mixed with three to four times its mass of new material of appropriate composition. Based on the estimated mass of the sediment derived from anorthosite with the mass balance equations, the total mass of sediments after this addition is slightly greater than the highest estimates of the total mass of sediments and sedimentary rocks in the crust (Garrels and MacKenzie, 1971; and Li, 1972). The 1 : 3 (X = 0.75) and 1 : 4 (X = 0.80) mixing ratios thus represent the maximum amount of new material it would be reasonable to add to the sedimentary mass.

At these mixing ratios, the composition of the material that must

be added to the anorthosite-derived sediment has a silica to alumina mass ratio within the range of that of rhyolites, rhyodacites, and quartz monzonites. These, however, are generally low in magnesium particularly, and iron, to an extent, with respect to the required compositions, and somewhat rich in alkalis. The appropriate compositions are also approached by quartz diorites, which are somewhat deficient in alkalis. Ultramafic rocks have favorable silica to alumina ratios, and small proportions of these could provide the necessary amounts of magnesium and iron. It is thus possible to bridge the compositional gap between an anorthositic primordial crust and average Precambrian sediments with a mixture of silica-rich alkali volcanic or plutonic rocks and ultramafic rocks.

This change in the chemical character would have had to occur between 3500 million years before present, when greenstone belt volcanic activity commenced to add new material to the sedimentary mass, and the end of the Precambrian, at which time the character of the sediments had changed to the average composition estimated by Reilly and Shaw.

Definite geochemical trends can be predicted for sedimentary rocks within the Precambrian if this change has occurred. The ratio of Al_2O_3 to SiO₂, and the proportion of CaO in Precambrian sediments should decrease with decreasing age. The proportions of Fe, Na₂O, and K₂O should increase with decreasing age, as should the ratios K₂O : Na₂O, MgO : CaO, and Fe : MgO. If the primordial crust were anorthositic, these chemical trends should be quite marked in Precambrian sediments.

Two problems hinder the evaluation of these trends. The first is the problem of determining the pre-metamorphic nature of most Precambrian rocks. It is usually quite difficult to distinguish metavolcanic rocks from metasedimentary rocks, and for rocks that have experienced very high

degrees of metamorphism, it may be impossible to distinguish rocks of volcanic or sedimentary pre-metamorphic character from metamorphosed plutonic rocks. These distinctions are often made on the basis of the chemistry of the metamorphic rocks, so that metasediments substantially different from typical modern sediments may not be identified as such, and these chemically "different" metasediments are the ones that would be needed to identify chemical trends. The most extensive compilations of chemical data for Precambrian rocks do not make a distinction between metasediments and metavolcanics (Ronov and Migdisov, 1971; Ronov, 1972; and Shaw et al, 1967).

The second problem is that of determining ages of Precambrian sediments and metasediments for which geochemical data are available. Compilations of data for Canadian shield Precambrian sediments (Reilly and Shaw, 1967) make no age distinctions, while estimates of Canadian shield geochemistry that distinguish between Archean and Proterozoic rocks rocks do not distinguish these rocks by pre-metamorphic character. This bimodal time distinction, even when made, is not sufficiently sensitive to evaluate the chemical trends we seek. In each of the two time periods, chemical data is averaged over a range of ages in excess of 1.5 billion years. The chemical changes for which we seek to evaluate trends may be completed entirely within one of these time periods.

The data of Ronov and Migdisov are compiled for four time periods within the Precambrian: Azoic (older than 3500 million years), Archeozoic (3500 to 2700 million years before present), and two subdivisions of Proterozoic (2700 to 1400 million years before present, and 1400 to 600 million years before present). These time distinctions are also not sufficiently sensitive to identify the chemical trends that need to be

evaluated, due to the length of the Archeozoic and early Proterozoic divisions.

The data of Ronov and Migdisov can be roughly compared to the predicted trends. Their data show a decrease in the proportion of K_2^0 in clays and shales with greater age, as predicted. The data also indicate a decrease in the ratio of $Al_2^0_3$ to SiO_2 in clays and shales with greater age, and an increase in the amount of iron in clays and shales; both of these trends are counter to those predicted for an anorthositic primordial crust. These trends are based on geochemical data for sedimentary and volcanic rocks in the Archeozoic and the two divisions of the Proterozoic. The trends do not support an anorthositic crustal model, but as noted above, the data are not sensitive enough to accurately evaluate the predicted trends.

Ronov (1972) has published trends for the chemical character of the continental erosion surfaces through geologic time. These cannot be used to evaluate the trends predicted for the anorthositic model, as they are based only in part on observed chemical data. The trends, particularly those for the early Precambrian, are derived instead from Ronov's own model of crustal evolution.

CONCLUSIONS

Application of a chemical mass balance equation to a modeled anorthositic crust produces a predicted sedimentary suite of 55% shale or clay, 1 to 2% carbonate-rich iron formation, 23% limestone, 1 to 2% evaporites, and 20% aluminum-rich rock. This suite is unlike modern proportions of sedimentary rock types, and should be recognizable if it occurs as an ancient deposit.

Lithologies of the only sedimentary or metasedimentary rocks yet discovered of appropriate age and tectonic setting to represent the sediments weathered from a world-wide primordial crust, the earliest sediments in Greenland, indicate a more siliceous and more alkali primordial composition than the anorthosite modeled by Shaw.

The suggested anorthositic primordial crust is sufficiently distinct in chemical character that it would have a marked effect on the chemistry of early sediments as it is weathered and recycled. The geochemical trends predicted for the evolution of the sedimentary mass from this distinctive initial composition to the average composition of Precambrian sediments are not consistently observed in ancient sediments. The data on the chemistry of Precambrian sediments are not, however, sufficiently sensitive to accurately identify the predicted trends.

This study indicates that the choice of an anorthositic composition for a primordial world-wide crust predicts a suite of sedimentary rock types for the earliest sediments that is not consistent with observations of the oldest known continentally derived and continentally deposited sediments; these indicate a more granitic primordial crustal composition. If the predicted suite does occur, or if it has imparted a distinctive chemical character to ancient sediments through recycling, the sediments that would substantiate an anorthositic primordial composition have not been located, or have not been properly identified.

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APPENDIX

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APPENDIX.

Sedimentary suites that do not balance with an anorthositic crust.

All mass balance calculations were made with sedimentary suites that included one or more carbonate rocks, and one or more silica or alumina-silica rocks, i.e. shales, graywackes, clays, or sandstones. Some calculations were made with suites that excluded evaporites. A comparison of the results of these calculations with the results of calculations for the same suites with evaporites included showed that the evaporites had little effect on the determination of coefficients for the sedimentary rock types; their presence or absence was noticable only in the values of sodium, chlorine, and sulfate residuals.

A number of calculations were made with potassium and titanium excluded from the component balances. Comparison of the results of these calculations with the results of recalculations of the same suites with these two components included in the balance demonstrated that the inclusion or exclusion of potassium and titanium had little effect on the estimation of the rock-type coefficients.

Seawater was included in all calculations.

No sedimentary suites that included a sandstone balanced satisfactorally with an anorthositic crust. For suites that included both a sandstone and a clay or shale, with one exception, the mass balance estimates produced negative coefficients for the sandstone, in the range -0.20 to -0.30, depending on the other rock types in the suite. With respect to the mass balance equation, this means that balance was achieved by having the sandstone on the reactants or source side of the equation rather than on the products side of the equation. The exception

was a suite containing a sandstone, a graywacke, and a shale. This suite balanced with graywacke coefficients in the range of -1.48 to -0.846. Suites that included ironstones with a sandstone and a shale produced negative coefficients for the ironstones as well as for the sandstone.

Suites that included a graywacke and a shale, without a quartz sandstone, balanced with negative graywacke coefficients. Balances calculated with Archean graywacke and Archean shale were less satisfactory, as the coefficients estimated for the graywacke were even more negative than those estimated for modern graywackes. Ironstones included in shale plus graywacke suites also had negative coefficients.

Suites calculated with shales, and with sandstones, ironstones and graywackes excluded, generated positive coefficients for all rock types. These balances were unsatisfactory due to high residual values, with best values of SSR in the range 11.8 to 24.1. The results for these calculations showed high negative Al_2O_3 residuals, indicating that the anorthosite was rich in aluminum compared to the estimated sedimentary suite, and high positive SiO_2 residuals, which indicated a silica deficiency in the anorthosite. When graywackes were substituted for shales in these suites, the adverse alumina and silica residuals were accentuated.

Addition of an ironstone to suites containing a shale as the only other silica rock generated negative ironstone coefficients, but silica residuals were reduced.

The first reasonable mass balances were produced by adding a hypothetical aluminum-rich rock to the sedimentary suites, representing an aluminum ore of a hydroxide type. This technique did not work equally well with all sedimentary suites. Those that included a sandstone, a

shale, and alumina rock generally produced negative shale coefficients. Suites that included a shale or clay and alumina rock, and excluded a sandstone produced positive coefficients for both the shale and the alumina rock, with SSR values below 2.0. The alumina rock technique did not work for either Archean shales or Archean graywackes, or modern graywackes, or any combination of these rock types.

Ironstones in these first reasonable balances had positive or negative coefficients depending on the choice of the type of ironstone and the clay or shale. Dolomite usually had negative coefficients, but not always in excess of the standard deviation for the dolomite coefficient.

Sedimentary suites with successful mass balances included a clay or shale, alumina rock, an ironstone, limestone with or without dolomite, evaporites, and seawater. The results of the successful mass balance calculations are tabulated in Tables 5 through 10.

