

# Data of Geochemistry

## *Sixth Edition*

*Chapter S.* Chemical Composition of Sandstones—Excluding Carbonate and Volcanic Sands

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-S



# Data of Geochemistry

## *Sixth Edition*

MICHAEL FLEISCHER, *Technical Editor*

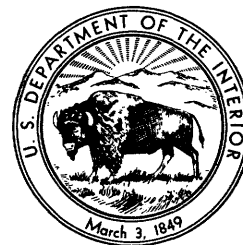
### *Chapter S.* Chemical Composition of Sandstones—Excluding Carbonate and Volcanic Sands

By F. J. PETTIJOHN

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-S

*Representative analyses, minor-element content, and estimated averages are given for both major classes of sandstones and for sandstone as a whole*



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# DATA OF GEOCHEMISTRY, SIXTH EDITION

Michael Fleischer, *Technical Editor*

The first edition of the Data of Geochemistry, by F. W. Clarke, was published in 1908 as U.S. Geological Survey Bulletin 330. Later editions, also by Clarke, were published in 1911, 1916, 1920, and 1924 as Bulletins 491, 616, 695, and 770. This, the sixth edition, has been written by several scientists in the Geological Survey and in other institutions in the United States and abroad, each preparing a chapter on his special field. The current edition is being published in individual chapters, titles of which are listed below. Chapters already published are indicated by boldface.

- CHAPTER A. The chemical elements
- B. Cosmochemistry
- C. Internal structure and composition of the Earth
- D. Composition of the earth's crust
- E. Chemistry of the atmosphere
- F. **Chemical composition of subsurface waters**, by Donald E. White, John D. Hem, and G. A. Waring
- G. **Chemical composition of rivers and lakes**, by Daniel A. Livingstone
- H. Chemistry of the oceans
- I. Geochemistry of the biosphere
- J. Chemistry of rock-forming minerals
- K. **Volcanic emanations**, by Donald E. White and G. A. Waring
- L. Phase equilibrium relations of the common rock-forming oxides except water
- M. Phase equilibrium relations of the common rock-forming oxides with water and (or) carbon dioxide
- N. Chemistry of igneous rocks
- O. Chemistry of rock weathering and soils
- P. Chemistry of bauxites and laterites
- Q. Chemistry of nickel silicate deposits
- R. Chemistry of manganese oxides
- S. **Chemical composition of sandstones—excluding carbonate and volcanic sands**, by F. J. Pettijohn
- T. **Nondetrital siliceous sediments**, by Earle R. Cressman
- U. Chemical composition of shales and related rocks
- V. Chemistry of carbonate rocks
- W. Chemistry of iron-rich rocks
- X. Chemistry of phosphorites
- Y. **Marine evaporites**, by Frederick H. Stewart
- Z. Continental evaporites
- AA. Chemistry of coal
- BB. Chemistry of petroleum, natural gas, and miscellaneous carbonaceous substances
- CC. Chemistry of metamorphic rocks
- DD. Abundance and distribution of the chemical elements and their isotopes
- EE. Geochemistry of ore deposits
- FF. Physical chemistry of sulfide systems
- GG. The natural radioactive elements
- HH. Geochronology
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## DATA OF GEOCHEMISTRY

### CHEMICAL COMPOSITION OF SANDSTONES—EXCLUDING CARBONATE AND VOLCANIC SANDS

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#### ABSTRACT

Sandstones range from virtually pure silica to complex chemical compositions; some, the graywackes, for example, are not greatly different from many igneous rocks in bulk composition.

Forty-eight representative analyses of the principal classes of sandstone (orthoquartzites, subgraywackes, graywacke, and arkose) are tabulated. From about 150 published analyses an average of the major elements in each class and an arithmetic mean for sandstone as a whole have been calculated. The data on minor and trace elements have been summarized. An approximate average has been estimated for these elements. Sample inadequacies do not justify calculated averages or standard deviations.

Data are given to show relation of chemical composition of sandstones to their grain size and mineral composition. In general, silica diminishes with decreasing grain size, whereas alumina,  $K_2O$ , and water increase. The variation of other constituents is less dependent on size. The detrital components of sands range from nearly pure quartz to mixtures of quartz, feldspar, and rock particles; hence sandstones show simple to complex chemical compositions. The composition is a function not only of the detrital components but also of the cement. The common cements, quartz and calcite, lead to enrichment in silica or in lime and carbon dioxide.

The composition is also a function of source rock, completeness of weathering, diagenesis, and other postdepositional changes. These factors are discussed, but supporting data are not generally available. The distribution of the chemical elements in the minerals of sandstones is discussed in general terms; detailed analysis is not possible from presently available data.

#### INTRODUCTION

##### GENERAL REMARKS

The sandstones belong to the "resistates"—that group of clastic sediments which originate by weathering or breakdown of the parent rock and which are the transported or washed residues resulting from this disintegration. Consequently they tend to consist of the most resistant materials—the chemically more inert and mechanically more durable minerals. The washing process mechanically separates the finer secondary products of weathering, including the clay minerals, from the coarse, little altered resistant minerals which survived the weathering processes.

Chief of the surviving minerals of sand size is quartz. Hence quartz is the most prominent constituent of most sands and sandstones and indeed is almost the sole constituent of many sands. The chemical composition of such sands is, therefore, essentially silica and little else. Incomplete weathering or incomplete washing or both lead to formation of immature sands, such as arkose and graywacke. In such sands the quartz is diluted by undecomposed rock-forming silicates, such as feldspar, and the finer products of weathering—the aluminous clay minerals. These sands are, therefore, chemically more complex and contain alumina and other oxides. Even the pure quartz sands, however, may be bound together by chemical cements, such as calcite, which alter their bulk composition. Sands may also be made chemically more complex by biochemical contaminants such as shell debris.

The bulk chemical composition of a sandstone, therefore, is a function of the composition of the source rocks, the nature and maturity of the weathering processes, the effectiveness of the winnowing or washing out of the finest weathering products, the quantity and nature of the introduced cement and other changes during diagenesis, and on the presence or absence of biochemical or other contaminants.

Although the bulk chemical composition of most sandstones is characterized by overwhelming dominance of silica, alumina is commonly an important constituent. The orthoquartzites of Krynine (1948, p. 149) and others are the high-silica sands that contain less than 3 percent alumina. The subgraywackes and lithic sandstones and subarkoses which are characterized by a considerable proportion of detrital rock particles—mainly argillite, slate, phyllite, shale, and siltstone—and some interstitial clay contain from 3 to 10 percent of alumina. The arkoses and the graywackes contain 10 to 20 percent or higher of alumina. In the arkoses the alumina is largely in the detrital feldspars, in the graywackes it is in both the detrital feldspars and rock particles and in the matrix. The alkalis are highly variable, being absent in the orthoquartzites and



important in the graywackes and arkose. Sodium oxide apparently is contained in feldspars, as is  $K_2O$  which, however, is also in rock particles and the clay minerals of the matrix. The quantities of lime, silica, and carbon dioxide are also highly variable, depending on the quantity and kind of cement in the sandstone. The percentages of iron oxide and magnesia are variable and are rather high in the graywackes. In certain rocks the iron is related to siderite cement or its oxidation products, and in such rocks its concentration bears no relation to magnesia content.

In general the sandstones are more highly differentiated chemically than are the shales. The silica content of the sandstones varies widely, ranging from less than 50 percent to more than 99 percent. Common shales exhibit no such range. The alumina content likewise ranges from nothing to more than 20 percent in the sandstones; shales are invariably aluminous and hence show not only less variation in this constituent but also less variation in the related  $Na_2O$  and  $K_2O$ . Both shale and sandstone show wide fluctuations in content of silica, lime, and carbon dioxide owing to biochemical admixtures of silica and calcium carbonate, and for the sandstones, owing also to introduction of such materials as intergranular cement.

#### EVALUATION AND SELECTION OF ANALYSES

The analyses utilized in this study were obtained mostly from readily available publications. Stratigraphic nomenclature used is that of the published sources and does not necessarily conform to that of the U.S. Geological Survey.

Although many sandstone analyses have been published, comparatively few can be used. Good and complete analyses are rare. Published analyses are commonly defective in one or more particulars. Many are incomplete, even for the major constituents. The iron is commonly reported as ferric oxide even though ferrous iron is present. The alkalies are commonly omitted, as is also titania. Combined water is rarely determined—too commonly only “loss on ignition” is reported. Carbon dioxide is not determined in many analyses, even in sandstones that are known to be calcareous. Some analyses, less than satisfactory, have been used because none better could be found. In all, fewer than 200 analyses were found to be acceptable.

The published analyses, even the good ones, are not necessarily representative of sandstones. They are commonly made because the rock was of special economic interest as a source of silica or as a building stone; or the rock is an unusual or rare type, perhaps glauconitic or phosphatic. It is unlikely, therefore, that the chemical composition of the “average sand-

stone” could be ascertained merely by averaging all available analyses no matter how complete.

The analyses selected as representative of certain classes of sandstone were, insofar as possible, the more complete analyses. They were also analyses of rocks for which some petrographic data or a photomicrograph were given, so that some reasonable assignment to the proper petrographic class could be made. Analyses supplemented by modal or normative compositions were used in preference to those without. Sandstones for which trace-element analyses were available were preferred to those without such supplementary data. This choice was, of course, rarely possible.

Owing to paucity of material some very old analyses were used, both in computing averages and in the tables of representative analyses. The quality of some of these are suspect, but scarcity of chemical data made their inclusion necessary.

#### RELATION OF CHEMICAL COMPOSITION TO GRAIN SIZE

Texture and chemical composition of clastic sediments are not independent variables. This has been clearly shown by analyses of various size fractions of the same sediment. Analyses such as those published by Grout (1925) and Boswell (1919, p. 33) show the silica content to diminish as grain size decreases, whereas  $K_2O$  and alumina content rise with decrease in grain size. These changes reflect the changing proportions of potassium-bearing clay materials and detrital quartz. The chemical composition, therefore, is in part dependent on the textural definition of the detrital sediment in question. Chemical analyses of two clastic sediments are comparable only if the two materials are texturally equivalent. These relations are further shown by comparing the chemical composition of the silt and the clay fractions of the same glacial lake varve (Eskola, 1932, p. 14). The differences are of the same kind as those shown by Grout. A comparison of Clarke's (1924) average sandstone, average Mississippi River silt, and average shale (table 1) reveal similar texturally controlled variations in bulk composition. As can be seen in table 1, decreasing grain size is correlated with decrease in silica and increase in alumina, total iron, magnesia,  $K_2O$ , combined water, titania, and organic matter. Lime and carbon dioxide are variable depending on nature and quantity of the cement.

The chemical composition of sands and sandstones is, therefore, in considerable part a matter of definition. As the chemical composition and the texture of clastic sediments are not independent variables, the definition of what is included or excluded in “sand” or “sandstone” will modify in appreciable measure the chemical

TABLE 1.—Chemical analyses of coarse-, medium-, and fine-grained clastic sediments

	A	B	C
SiO <sub>2</sub> .....	78.66	69.96	58.38
Al <sub>2</sub> O <sub>3</sub> .....	4.78	10.52	15.47
Fe <sub>2</sub> O <sub>3</sub> .....	1.08	3.47	4.03
FeO.....	.30		2.46
MgO.....	1.17	1.41	2.45
CaO.....	5.52	2.17	3.12
Na <sub>2</sub> O.....	.45	1.51	1.31
K <sub>2</sub> O.....	1.32	2.30	3.25
H <sub>2</sub> O+.....	1.33	1.96	3.68
H <sub>2</sub> O-.....	.31	3.78	1.34
TiO <sub>2</sub> .....	.25	.59	.65
P <sub>2</sub> O <sub>5</sub> .....	.08	.18	.17
MnO.....	Trace	.06	Trace
CO <sub>2</sub> .....	5.04	1.40	2.64
SO <sub>2</sub> .....	.07	.03	.65
Cl.....	Trace	.30	-----
BaO.....	.05	.08	.05
SrO.....	Trace	Trace	None
Organic.....	-----	.66	.81
	100.41	100.50	100.46

<sup>1</sup> Includes organic matter.

<sup>2</sup> Total includes ZrO<sub>2</sub>, 0.5; F, 0.07; S, 0.07; Cr<sub>2</sub>O<sub>3</sub>, 0.01; V<sub>2</sub>O<sub>5</sub>, 0.02; NiO, 0.017; CuO, 0.0043; ZrO<sub>2</sub>, 0.0010; As<sub>2</sub>O<sub>3</sub>, 0.0004; PbO, 0.0002; less O = F<sub>2</sub>S<sub>2</sub>, 0.12.

A. Sandstone, composite of 253 samples, H. N. Stokes, analyst. Clarke (1904, p. 20).

B. Mississippi River silt, composite of 235 samples. G. Steiger, analyst. Steiger and Clarke (1914, p. 59).

C. Shale, composite of 78 samples, H. N. Stokes, analyst. Clarke (1904, p. 20).

composition. Sand has been variously defined. Cayeux, for example, defines sand as detrital materials ranging in diameter between 0.05 and 5.0 mm whereas Hopkins sets limits of 0.032 and 1.0 mm. (See Truesdell and Varnes, 1950.) Such definitions, though laudable, are not sufficient even if agreement on the proper limits could be reached. One needs also to specify the permissible admixtures of materials greater or smaller than the sizes agreed upon. Must 50 percent or more fall between the agreed limits? Or must only the average or median fall within these limits? Obviously if a large percentage of silt or clay is present, the bulk chemical composition will be different from those sands without such admixtures. The chemical composition is, therefore, in part arbitrarily set by choice of class limits and by the permissible variation in sorting. As size analyses are seldom given, one is unable to say whether many rocks labeled "sandstones" and analyzed as such truly meet even the more generally accepted definitions of this rock.

## CHEMICAL COMPOSITION AND CLASSIFICATION OF SANDSTONES

### GENERAL REMARKS

As noted, the "average" chemical composition of a given rock type is a statistical mean of what geologists characteristically designate as the rock in question. For example, average graywacke is the average of what most workers call "graywacke." As the class limits are seldom agreed upon, are rarely well defined, and often are not specified, any norms or averages based on published analyses must be something of a statistical mean of the prevailing concept of the rock class in question and not an objectively and statistically

controlled sample of a well-defined rock class. Lack of precise petrographic data, even of many chemically analyzed materials, makes it impossible to reclassify most materials into better defined groups. It may also be that the materials analyzed are not average or normal materials but are analyzed rocks that tend either to be "types" which correspond most closely to preconceived norms or are problematic rocks of uncertain character. From the rocks tending toward "types" the collector tends to discard "abnormal," less "typical" materials for analysis; from the "problematic" rock material the geologist hopes the analysis will tell him what the rock is. For obvious reasons the second cannot be utilized in computing averages and it is also obvious that the first may give rise to misleading averages. Few "bulk" samples, collected as a mining engineer would collect them, have been analyzed. Hence our knowledge of the chemical composition of the rocks of the earth's crust and of sandstones in particular is incomplete and inadequate.

### CLASSIFICATION OF SANDSTONES

The bulk chemical composition of sandstones can be understood only if the fabric and mineralogical constitution of the sandstone are known. Sands consist of detrital elements packed together in such a manner as to form a grain-supported framework stable in the gravitational field. These framework elements may or may not be bound together by a cement. Neither the detrital elements nor the cement may be in chemical equilibrium with one another and hence wide ranges in composition are possible.

Sandstones may be classified on the basis of the kinds of detrital elements present.<sup>2</sup> The principal detrital materials of the noncarbonate sands are (1) quartz, (2) feldspars, and (3) rock particles. Sands consisting solely of quartz are the high silica sands—the so-called orthoquartzites—with silica content in excess of 95 percent. The feldspathic sands and the arkoses consist mainly of feldspar and quartz and are more complex in chemical composition. They contain much alumina, lime, Na<sub>2</sub>O, and K<sub>2</sub>O, as well as silica. The lithic sands—those composed of sand-sized rock particles in addition to quartz—vary widely in composition depending on the dominant lithic elements present. These may be fine-grained sediments, such as chert, shale, and siltstone, low-rank metamorphic rocks such as slate and phyllite, or aphanitic igneous rocks of various kinds.

<sup>2</sup> This is not the place to review the whole problem of sandstone classification. The interested reader is referred to recent papers by Folk (1954, 1956), Dapples, Krumbein, and Sloss (1953), Turnau-Morawska (1956), Bokman (1955), Tallman (1949), Packham (1954), Pettijohn (1954), and others. The four main classes here defined are recognized by all writers, but their proper designation or defining limits are still subjects of debate.

The carbonate sands, those composed of mechanically sorted and segregated carbonate grains—such as oölites and bioclastic debris—are excluded from this section. Though truly sandstones in fabric and other geometrical properties, they are commonly classed as limestones by the field geologist and hence have been included with the limestones and related carbonate rocks. For the most part the volcanic sands and sandstones also have been omitted as they are traditionally treated as volcanic or pyroclastic deposits. Inasmuch as all gradations exist between carbonate and noncarbonate sands and between volcanic and nonvolcanic sands, some transitional types have been included to indicate the changes in bulk chemical composition to be anticipated in such hybrid rocks.

Graywackes constitute another major class of sands. Although variously defined, the classic graywackes of the Harz (Helmbold, 1952; Mattiat, 1960) and the graywackes of the field geologists are primarily feldspathic or lithic sandstones with a prominent detrital matrix—a matrix of silt- and clay-sized materials having the mineralogical and chemical composition of a shale or slate. However, unlike other sandstones, graywackes show no sharp break in grain size between the “framework fraction” and the “matrix.” The bulk chemical composition of most graywackes can be approximated by taking two parts of shale and one part of either arkose or lithic sandstone. Hence graywackes are not only high in  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ , but also high in iron and  $\text{MgO}$ . In composition they differ only slightly from granodiorite (Taliaferro, 1943, p. 137).

The chemical composition of the orthoquartzites, arkoses, and lithic sandstones may be greatly modified by the introduction of various void-filling cements. The silica content may be augmented by the introduction of silica. Carbonate cements are common and are indicated by a high carbon dioxide content as well as by an increased lime content (or magnesia or  $\text{FeO}$  content if dolomite or siderite is present).

Hence sandstones range from a simple bulk composition—one oxide such as silica—to complex compositions indistinguishable from igneous rocks of silicic to intermediate composition. In general the dominant oxide is silica; next in importance is alumina (in the feldspathic and lithic sands) or lime and carbon dioxide (in the calcareous sands). The common rock-making elements—iron, magnesium, calcium, sodium, and potassium—are all major constituents of the arkosic and lithic sands. Only in a few rare unusual sand types do the minor components such as  $\text{BaO}$ ,  $\text{P}_2\text{O}_5$ , or  $\text{SO}_3$ , become major constituents. These rare sands owe their unusual composition to special types of introduced cement, such as barite or anhydrite, or to uncommon

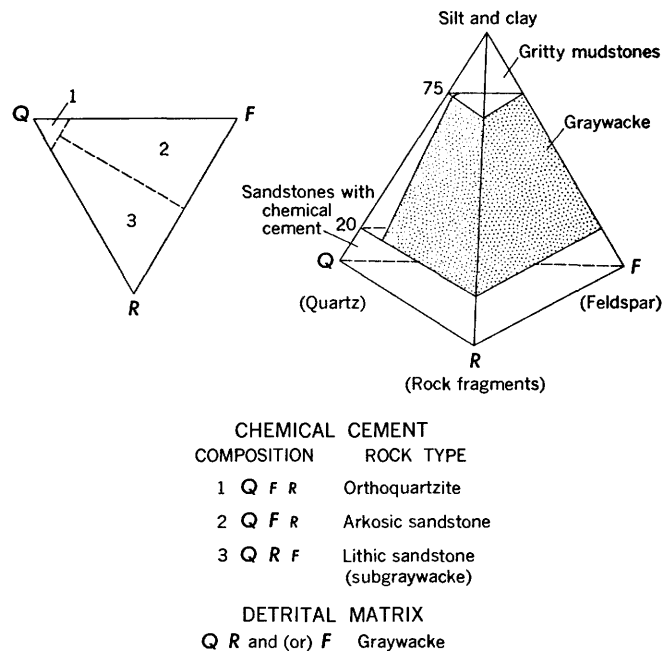


FIGURE 1.—Petrographic classification of sandstones. Modified from Pettijohn (1954).

framework constituents, such as glauconite or phosphatic debris.

The relations of the common sandstone types to one another are shown graphically in figure 1. In the following sections sandstone analyses have been selected to illustrate these major sandstone types and to show the range in composition exhibited by these types, as well as the transitional or intermediate varieties. These analyses were chosen to show the variations in the bulk composition which are related both to the differing types of framework elements and the differing types of cementing materials. Analyses were largely selected from published papers in which a good petrographic description, preferably with modal analyses and photomicrograph, is given.

#### MAJOR-ELEMENT COMPOSITION OF SANDSTONES

##### ORTHOQUARTZITES

The most mature sands consist of detrital quartz and little else. Hence chemically they are nearly pure silica. In fact, they constitute the greatest concentrations of this material in the crust of the earth and exceed in volume and purity any other deposits of silica. Such are the glass sands. Cementation of these sands with silica produces orthoquartzites (Krynine, 1948). The cement, commonly deposited in crystallographic continuity on the detrital grains, welds the rock into a truly quartzitic whole without any significant alteration of the bulk composition. Analyses of representative orthoquartzites and other highly mature sandstones are given in table 2. As can be seen from the table, all

TABLE 2.—*Chemical analyses of orthoquartzites*

	A	B	C	D	E	F	G	H	I	J
SiO <sub>2</sub> -----	98.87	95.32	97.58	97.36	98.91	83.79	99.54	99.40	97.30	93.13
Al <sub>2</sub> O <sub>3</sub> -----	.41	2.85	.31	.73	.62	.48	.35	.20	1.40	3.86
Fe <sub>2</sub> O <sub>3</sub> -----	.08	.05	1.20	.63	.09	.063	.09	.01	.30	.11
FeO-----	.11			.14						.54
MgO-----	.04	.04	.10	.01	.02	{ .05 8.81	.06	.01	.03	.25
CaO-----		Trace	.14	.04			.19	<.01	<.05	.19
Na <sub>2</sub> O-----	.08		.10	.08	.01			.08	<.05	
K <sub>2</sub> O-----	.15	.30	.03	.19	.02			Trace	.20	
H <sub>2</sub> O+-----	.17	{		.54			.25	.04		
H <sub>2</sub> O-----				.14				.01		
TiO <sub>2</sub> -----				.05	.05		.03	.02	.23	
P <sub>2</sub> O <sub>5</sub> -----				.02				None		
MnO-----				.01				Trace	.003	
ZrO <sub>2</sub> -----								<.01	.06	
CO <sub>2</sub> -----						1 6.93				
Ignition loss-----		1.44	.03		.27			.28		1.43
Total-----	99.91	100.00	2 99.62	99.94	99.99	3 100.13	100.51	4 100.05	99.57	99.51

<sup>1</sup> Calculated.<sup>2</sup> Including SO<sub>3</sub>, 0.13.<sup>3</sup> Includes organic matter, 0.006.<sup>4</sup> Includes Cr<sub>2</sub>O<sub>3</sub>, 0.00008; BaO and SrO, none; NiO, less than 0.0001; CuO, less than 0.00027; CoO, less than 0.0002.

- A. Mesnard Quartzite, Precambrian, Marquette County, Mich. R. D. Hall, analyst. Van Hise and Leith (1911, p. 256).  
 B. Lorrain Quartzite, Precambrian, Plummer Township, Ontario, Canada. M. F. Conner, analyst. Collins (1925, p. 68).  
 C. Sioux Quartzite, Precambrian, Sioux Falls, S. Dak. Rothrock (1944, p. 151).  
 D. Lauhavuori Sandstone (Cambrian(?)), Tiiliharju, Finland, Pentti Ojanperä, analyst. Simonen and Kuovo (1955, p. 79). Quartz 70-75; feldspar 0.1-1.4; rock fragments 0.1-5.6; silica cement 13-20.

E. St. Peter Sandstone, Ordovician, Mendota, Minn. A. William, analyst. Thiel (1935, p. 601).

F. Simpson Sand, Ordovician, Cool Creek, Okla. Buttram (1913, p. 50).

G. Tuscarora Quartzite, Silurian, Hyndman, Pa. Fetteke (1918, p. 263).

H. Oriskany Sandstone, Devonian, Berkeley Springs quarry, Pennsylvania Glass Sand Corp., Sharp-Schurtz Co., analysts. Analysis supplied courtesy of Pennsylvania Glass Sand Corp.

I. Mansfield Formation, basal Pennsylvanian, Crawford County, Ind. M. E. Collier, R. K. Leininger, R. F. Blakely, analysts. Computed mineral composition: Quartz 95.3; orthoclase 1.2; kaolin 3.0; ilmenite 0.3. Murray and Patton (1953, p. 28).

J. Berea Sandstone, Mississippian, Berea, Ohio, N. W. Lord, analyst. A proto-quartzite. Cushing, Leverett, and Van Horn (1931, p. 110).

## LITHIC SANDSTONES (SUBGRAYWACKES)

oxides other than silica may make up as little as 0.5 percent of the rock, except for the calcite-cemented varieties. The finer grained varieties, transitional to siltstone, and those which verge on subarkoses and protoquartzites, have appreciable quantities of alumina, alkalis, and alkaline earths.

Some mature quartz sands are cemented with calcite or other carbonates. Introduction of such cements alters the bulk composition. An analysis of calcareous sandstone is also given in analysis F, table 2. The geometry of the sand sets a limit to the quantity of CaO and CO<sub>2</sub> present. The cementing components cannot exceed the volume of the original pore space and hence cannot exceed about 35 to 40 percent of the rock. A content in excess of this limit suggests the presence of detrital carbonate, such as shelly material, in addition to the cementing carbonates.

Cements other than silica or calcite are also known. Siderite-cemented sands show large quantities of FeO. If such a cement is oxidized, the Fe<sub>2</sub>O<sub>3</sub> content will be high and CO<sub>2</sub> nil. Other sands contain iron silicates or calcium phosphate either as cementing material, as granules, as oölites, or, for phosphate, as shell materials. Analyses of representative sandstones with such mineralogical complexities are given in table 9.

The heavy-mineral content of the orthoquartzites approaches the vanishing point. The trace amounts of zirconium and titanium reported by some analysts in these sands are probably contained in these minor accessory minerals.

The group of sandstones here designated "lithic sandstones" is a large and varied group of rocks that is not too well defined. Some authors have called them "lithic arenites" (Williams, Turner, and Gilbert, 1954, p. 294), "subgraywackes" (Pettijohn, 1949, p. 255; 1957, p. 316) "low-rank graywackes" (Krynine, 1948; Folk, 1954). To this group belong the molasse sandstones as defined by Cayeux (1929, p. 156) and here also are many or most of the coal measure sandstones commonly described by field geologists as "argillaceous grits." This is a large and important group of sandstones, forming according to some estimates, 35 percent of all sandstones (Krynine, 1948, p. 156).

Modal analyses of some sandstones of this group are given in table 3. As can be seen from the table, the sands are characterized by dominance of quartz; abundance of rock particles, mainly of fine-grained sedimentary and of low-rank metamorphic derivation; and general subordinate content of feldspar. The rocks are light gray if fresh, are rather friable and generally poorly cemented by calcite. Many are described as containing "clay" as "gangue" or matrix. The clay appears to be in part precipitated in the pores, in part trapped at the time of sedimentation, and in part merely squeezed and deformed detrital shale particles that are mistaken for pore fillings.

As shown in table 4, the bulk chemical composition of these rocks reflects their modal composition. Alumina is high, as in the arkoses and graywackes. Unlike the

TABLE 3.—Modal analyses of lithic sandstones (subgraywackes) and protoquartzites

	A	B	C	D	E	F	G
Quartz.....	65.4	30.9	60	60-65	50	32.0	50-80
Feldspar.....		10.0	2-10	1.5	3-5	2.2	Nil
Mica.....		.5	1-5	2-3		.2	<3
Rock fragments.....	10.6	33.0	15	30	40	43.0	30-50
"Clay" or matrix.....	6.8	5.5	20	5-10	10	6.9	<2
Silica cement.....	11.9		Trace		1	Trace	Present
Calcite cement.....	8.5	19.2	5-20	2-18		13.0	Nil

<sup>1</sup> 5-10 percent, my observation.

- A. Salt Wash Member of Morrison Formation (Jurassic), Colorado Plateau. Mean of 25 thin sections. Griffiths (1956, p. 25). Compare analysis A, table 4.  
 B. Frio Formation, Oligocene, Seeligson field, Jim Wells and Kleberg Counties, Tex. Average of 22 samples. Nanz (1954, p. 112). See analysis B, table 4.  
 C. Trivoli Sandstone, Pennsylvanian, Illinois. Siever (1949).  
 D. Bradford Sand, Devonian, Pennsylvania. Krynine (1940).  
 E. Oswego Sandstone, Ordovician, Pennsylvania. Krynine and Tuttle (1941).  
 F. Calcareous graywacke, Cretaceous, Torok, Alaska. Average of 3 samples. Krynine in Payne and others, (1951).  
 G. Pocono Formation, Mississippian, Pennsylvania. B. R. Pelletier (1957, Pocono paleocurrents: Unpublished Ph. D. thesis, The Johns Hopkins Univ., p. 26).

arkoses, however, these rocks have high contents of combined water, bound in the argillaceous detritus or in the clay matrix. They are unlike the graywackes, which also are rich in both combined water and alumina, in that  $K_2O$  generally exceeds  $Na_2O$ . The calcitic cement leads to a high  $CaO$  and  $CO_2$  content. Generally ferric iron exceeds ferrous iron—a relationship not characteristic of graywackes proper. High magnesia noted in some of these rocks suggests a somewhat dolomitic carbonate in the cement.

TABLE 4.—Chemical analyses of lithic sandstones (subgraywackes) and protoquartzites

	A	B	C	D	E	F	G	H
$SiO_2$ .....	84.01	65.0	56.80	51.52	92.91	47.75	40.35	74.45
$Al_2O_3$ .....	2.57	9.57	8.48	5.77	3.78	6.41	7.43	10.83
$Fe_2O_3$ .....	.17	1.59	1.67	2.43	Trace	2.39	3.27	4.62
$FeO$ .....	.26	1.08			.91			
$MgO$ .....	.67	.4	1.24	.95	Trace	4.48	10.28	1.30
$CaO$ .....	5.41	10.1	15.25	16.96	.31	18.75	12.00	.35
$Na_2O$ .....	.17	2.14	1.31	1.32	.34	1.20	.54	1.07
$K_2O$ .....	.86	1.43	1.46	1.90	.61	1.02	.93	1.51
$H_2O^+$ .....	.54	.82	.50	2.25		1.32	6.75	4.95
$H_2O^-$ .....	.19	.23		2.54	1.19			
$TiO_2$ .....	.05		.10	.32		.20	.30	.50
$P_2O_5$ .....	.04		Trace	.10		.10		Trace
$MnO$ .....	.04			.14				
$CO_2$ .....	4.65	6.9	12.95	13.34		17.78	17.80	Trace
$SO_2$ .....		.04		.52				
S.....	.02	.16						
Total...	<sup>1</sup> 99.73	<sup>2</sup> 99.54	99.76	100.06	100.05	<sup>3</sup> 101.40	99.65	99.58

<sup>1</sup> Includes  $Cl$ , 0.02;  $F$ , 0.01;  $BaO$ , 0.05.

<sup>2</sup> Includes  $C$ , 0.06;  $Cu$ , 0.002;  $V$ , 0.017;  $Zn$ , <0.03;  $Cr$ , 0.003.

<sup>3</sup> Sum given as 99.40 in original.

- A. Protoquartzite, Salt Wash Member of Morrison Formation, Jurassic. Composite of 96 unmineralized samples, Colorado Plateau. V.C. Smith, analyst. (Written communication, W. L. Newman, U.S. Geological Survey), compare analysis A, table 3.  
 B. Calcareous subgraywacke (lithic arenite), Oligocene (Frio Formation), Seeligson field, Jim Wells and Kleberg Counties, Tex. Nanz (1954, p. 114). Composite of 10 samples. (See analysis B, table 3.)  
 C. Calcareous subgraywacke (Molasse), Aquitanienne, Lausanne (Switzerland). Cayeux (1929, p. 161).  
 D. Calcareous subgraywacke (Molasse), Gränichen, Burghalde, Kt. Aargau (Switzerland). J. Jakob, analyst. Niggli and others (1930, p. 262).  
 E. Protoquartzite, Berea Sandstone (Mississippian), Berea, Ohio. L. G. Eakins, analyst. Clark (1890, p. 158).  
 F. Calcareous subgraywacke (?), Molasse burdigalienne, Voreppe (Isere). Cayeux (1929, p. 163).  
 G. Coal measure sandstone (calcareous subgraywacke?) (Carboniferous), Westphalian coal basin, France-Belgium (Hornu and Wasmes). Cayeux (1929, p. 227).  
 H. Coal measure sandstone (subgraywacke?) (Carboniferous) Westphalian coal basin, France-Belgium (Hornu and Wasmes). Cayeux (1929, p. 227).

## GRAYWACKES

Graywacke is a variety of sandstone which has been variously defined. A review of the nomenclatural problems has been given by Folk (1954), Williams, Turner, and Gilbert (1954, p. 297), McElroy (1954), and Pettijohn (1943; 1949, p. 243; 1957, p. 301). As here used the term graywacke denotes a sandstone consisting of quartz, feldspar, and rock particles of sand size embedded in a silt-clay-sized matrix (fig. 1). This is indeed the composition of the classic graywacke of the Harz (Helmhold, 1952; Mattiat, 1960) and is the composition of many other rocks which have been designated graywacke. Table 5 shows the modal analyses of graywackes.

Although there remains some uncertainty about the limits to be set and the guiding principles to be used in choice of such limits (priority, usage, or logical concepts), there are a considerable number of chemical analyses of graywacke in the literature which show a remarkable homogeneity of composition. Almost all these rocks would qualify as graywackes by any definition. Representative analyses are given in table 6. The mean composition of 61 analyses of graywackes is also given in table 7; see also table 14, analysis A.

TABLE 5.—Mineralogical composition of graywackes

[Based on modal analysis]

	A	B	C	D	E	F	G	H	I
Quartz.....	4	24	56	33	9	Trace	22	33	27
Feldspar.....	10	32	37	15	43	30	5	21	19
Rock fragments.....	50	19	7	3	10	13	26	7	30
"Matrix".....	32	( <sup>1</sup> )	( <sup>2</sup> )	45	25	45	47	33	21
Mica and chlorite.....		16			4			6	
Miscellaneous.....	2	8			* 4	* 10			3

<sup>1</sup> Not separately reported; 38 percent of rock is "clay and silt".

<sup>2</sup> Not separately reported.

\* Hornblende and pyroxene.

- A. Devonian lithic graywacke, Australia; average of 5. Crook (1955, p. 100).  
 B. Devonian and Mississippian (Tanner) feldspathic graywacke, Harz Mountains. Helmhold (1952, p. 256).  
 C. Jurassic and Cretaceous (Franciscan Formation) feldspathic graywacke, Calif.; average of 17 analyses. Taliaferro (1943, p. 135).  
 D. Precambrian feldspathic graywacke, Ontario; average of 3 analyses. Pettijohn (1943, p. 946).  
 E. Cretaceous (Purari) graywacke, Papua; average of 4. Edwards (1950b, p. 164).  
 F. Miocene tuffaceous (Aure) graywacke, Papua; average of 2. Edwards (1950a, p. 129).  
 G. Ordovician lithic (Martinsburg Shale) graywacke, Pennsylvania. McBride (1960).  
 H. Lower Mesozoic graywacke, Porirua district, New Zealand. Webby (1959, p. 472).  
 I. Harz Kulm graywacke. Mattiat (1960).

As can be seen from inspection of these tables, the graywackes have a lower silica content than do most sandstones—about the same or a little higher than is found in shales and related rocks—high alumina, high  $MgO$ , an excess of  $FeO$  over  $Fe_2O_3$ , and an excess of  $Na_2O$  over  $K_2O$ . The silica is present both in silicates and as free silica of detrital quartz. In the high content of alumina, lime,  $Na_2O$ , and  $K_2O$ , graywackes resemble arkose in which these constituents are present in feldspars. However graywackes differ from

TABLE 6.—*Chemical analyses of graywackes*

	A	B	C	D	E	F	G	H	I	J
SiO <sub>2</sub> .....	60.51	61.39	76.84	69.11	68.85	74.43	71.1	68.84	65.05	73.04
Al <sub>2</sub> O <sub>3</sub> .....	15.36	16.97	11.76	11.38	12.05	11.32	13.9	14.54	13.89	10.17
Fe <sub>2</sub> O <sub>3</sub> .....	.76	.39	.55	1.41	2.72	.81	Trace	.62	.74	.56
FeO.....	7.63	5.32	2.88	4.64	2.03	3.88	2.7	2.47	2.60	4.15
MgO.....	3.39	3.84	1.39	2.06	2.96	1.30	1.3	1.94	1.22	1.43
CaO.....	2.14	3.21	.70	1.15	.50	1.17	1.8	2.23	5.62	1.49
Na <sub>2</sub> O.....	2.50	2.78	2.57	3.20	4.87	1.63	3.7	3.88	3.13	3.56
K <sub>2</sub> O.....	1.69	1.25	1.62	1.76	1.81	1.74	2.3	2.68	1.41	1.37
H <sub>2</sub> O+.....	3.38	2.44	1.87	4.13	2.30	2.15	1.9	1.60	2.30	2.36
H <sub>2</sub> O-.....	.15	.06								
TiO <sub>2</sub> .....	.87	.62	Trace	.60	.77	.20	.26	.35	.28	.15
P <sub>2</sub> O <sub>5</sub> .....	.27	.19	Trace	.03	.06	.18	.10	.15	.08	.23
MnO.....	.16	.12	Trace	.17	.05	.04	.05	Nil	.11	.18
ZrO <sub>2</sub> .....		.07						.05		
CO <sub>2</sub> .....	1.01	.88			.08	.48	.12	.14	2.83	.84
SO <sub>3</sub> .....								.15		
S.....	.42	.15			.08	.12	Trace		.05	.10
Cr <sub>2</sub> O <sub>3</sub> .....		.01								
BaO.....		.06			Trace			.04		
C.....					.07	.17	.09			.17
Total.....	100.24	99.75	100.18	99.69	99.94	100.45	99.8	99.93	99.77	99.80

<sup>1</sup> Loss on ignition.

- A. Archean, Manitou Lake, Ontario. B. Brunn, analyst. Pettijohn (1957, p. 306).  
 B. Archean, Knife Lake, Minn. F. F. Grout, analyst. Grout (1933, p. 997).  
 C. Anniikean, Tyler slate, Hurley, Wis. H. N. Stokes, analyst. Diller (1898, p. 87).  
 D. Ordovician?, Rensselaer Graywacke, near Spencertown, N.Y. H. B. Wilk, analyst. Balk (1953, p. 824).  
 E. Upper Devonian and Lower Carboniferous, Tanner Graywacke, Scharzfeld, Germany. R. Helmbold, analyst. Helmbold (1952, p. 256).

- F. Carboniferous, graywacke from Stanley Shale, near Mena, Ark. B. Brunn, analyst. Pettijohn (1957, p. 319).  
 G. Lower Mesozoic, composite sample prepared by using equal parts of 20 graywackes exposed along shorelines between Palmer Head and Hue-Te-Taka, Wellington, New Zealand. J. A. Richie, analyst. Reed (1957, p. 16).  
 H. Jurassic and Cretaceous, Franciscan Formation, Quarry Oakland Paving Co., Piedmont, Calif. J. W. Howson, analyst. Davis (1918, p. 22).  
 I. Eocene, Olympic Mountains, Wash., near Solduc. B. Brunn, analyst. Pettijohn (1957, p. 306).  
 J. Carboniferous, Kulm, Steinbach, Frankenwald, Germany. Eigenfeld (1933, p. 58).

TABLE 7.—*Averages of analyses of graywackes*

	A	B	C	D	E	F
SiO <sub>2</sub> .....	66.75	65.50	69.7	64.67	68.1	69.7
Al <sub>2</sub> O <sub>3</sub> .....	13.54	12.57	14.3	13.41	15.4	14.3
Fe <sub>2</sub> O <sub>3</sub> .....	1.60	.69	1.0	1.24	1.0	1.9
FeO.....	3.54	5.63	2.5	4.53	3.4	2.4
MgO.....	2.15	3.30	1.2	3.23	1.8	1.8
CaO.....	2.54	4.69	1.9	3.04	2.3	1.3
Na <sub>2</sub> O.....	2.93	2.41	3.5	2.99	2.6	3.1
K <sub>2</sub> O.....	1.99	1.57	2.4	2.02	2.2	1.4
H <sub>2</sub> O+.....	2.42	.84	1.9	1.94	2.1	2.4
H <sub>2</sub> O-.....	.55	.14	.4	.20		
TiO <sub>2</sub> .....	.63	.53	.6	.57	.7	.5
P <sub>2</sub> O <sub>5</sub> .....	.16	.21	.2	.14	.2	.1
MnO.....	.12	.11	.1	.13	.2	.1
CO <sub>2</sub> .....	1.24	1.31	.1	2.15		.9
SO <sub>3</sub> .....	.25					
S.....	.07	.38				
BaO.....	.05	.02				
C.....	.08		.1			
Total.....	100.61	100.02	99.9	100.26	100.0	100.3

<sup>1</sup> Includes Cl, 0.02; SrO, 0.10.

- A. Average of 61 graywackes, by Pettijohn. See table 12, footnote 3.  
 B. Average of 7 South African graywackes (after Visser, 1956, p. 63).  
 C. Average of 14 New Zealand Mesozoic graywackes (after Reed, 1957).  
 D. Average of 12 Precambrian graywackes.  
 E. Average of 30 graywackes (Tyrrell, 1933, p. 26). Note that the value of Fe<sub>2</sub>O<sub>3</sub> in original is given as 3.4. This has been changed to 1.0.  
 F. Average of 17 Harz Mountain graywackes (Paleozoic). Data from Mattiat (1960, p. 277).

arkose in their excess of Na<sub>2</sub>O over K<sub>2</sub>O, in their high MgO content, and in both the high content and reduced state of the iron present. The iron and magnesium are in part combined in the chloritic materials of the paste-like matrix characteristic of most graywackes.

The excess of Na<sub>2</sub>O over K<sub>2</sub>O is one of the most singular chemical attributes of graywacke (fig. 2). In the associated shales, however, the converse is true (fig. 3). The Na<sub>2</sub>O seems to be tied up in the sodium-rich feld-

spars. In 30 analyses of New Zealand graywackes of various ages (Reed, 1957), the Na<sub>2</sub>O content ranges from 0.10 to 5.51 percent and is generally between 3 and 4 percent. Normative albite ranges from 1.0 to 50.0 percent and is generally 30 to 40 percent. Microscopic examination confirms the albitic nature of the plagioclase. Eighty-five to ninety percent of the feldspar in the Tanner Graywacke (Helmbold, 1952) is untwinned plagioclase (Ab<sub>90-97</sub>). Micrometric analysis discloses about 30 percent plagioclase; the rock, therefore, should contain 3.2 to 3.4 percent Na<sub>2</sub>O. The actual Na<sub>2</sub>O content of this rock ranges from 3.87 to 4.87 percent, which corresponds to 35 to 41 percent computed albite molecule; hence most of the Na<sub>2</sub>O must be in the feldspar. The origin of the albite is uncertain. It may have been produced by albitization of the plagioclase in the source rocks or of the feldspar in the graywacke after deposition. It may be related to the albitized feldspars commonly found in associated greenstones and spilites (Middleton, 1960, p. 1017).

Inasmuch as the associated shales are the finer decomposition products, they lack fresh feldspar and the Na<sub>2</sub>O/K<sub>2</sub>O ratio is less than one (fig. 3). Possibly the lithic graywackes have a Na<sub>2</sub>O/K<sub>2</sub>O ratio nearer to that of shales. The rock fragments most common in these graywackes—primarily slate, mudstone, phyllite, and related rocks—will be less rich in Na<sub>2</sub>O than the albitic feldspars of the feldspathic graywackes.

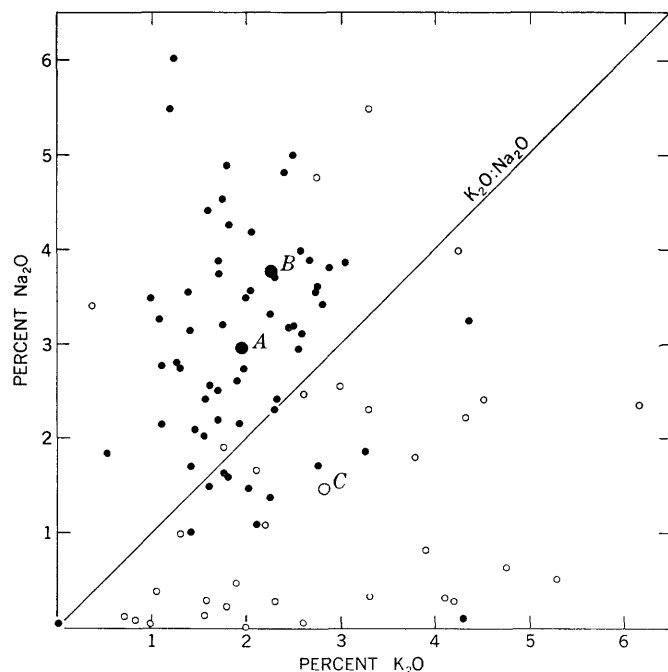


FIGURE 2.— $K_2O/Na_2O$  ratio in arkoses and graywackes. Solid black circles, graywackes; open circles, arkoses. Analyses essentially the same as those used for computing average graywacke and average arkose of table 12. See footnotes to table 12. A, Average graywacke. B, Composite New Zealand graywacke (Reed, 1957, p. 16). C, Average arkose.

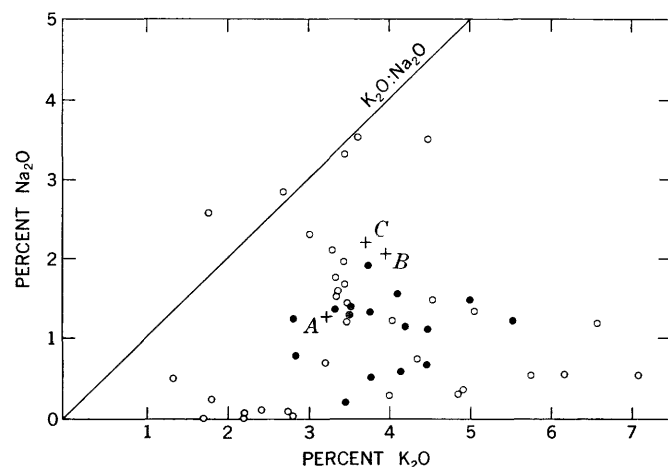


FIGURE 3.— $K_2O/Na_2O$  ratio in argillites, shales, and slates. From Pettijohn and Bastron (1959). Black circles, slates (after Dale, 1914, p. 51); open circles, Precambrian argillites (after Nanz, 1953, p. 53-54); crosses: A, Average shale (after Clarke, 1924, p. 34); B, Average Norwegian glacial clay (after Goldschmidt, 1954, p. 53); C, Composite New Zealand argillite (after Reed, 1957, p. 28). Compare with figure 2.

The graywackes are generally characterized by the reduced state of the iron; hence FeO greatly exceeds  $Fe_2O_3$ . This relationship has been attributed to deposition under reducing conditions but inasmuch as it characterizes most metamorphosed sediments, it may be indicative only of metamorphic reduction.

The other chemical characteristics of graywacke arise from the abundance of matrix materials in these

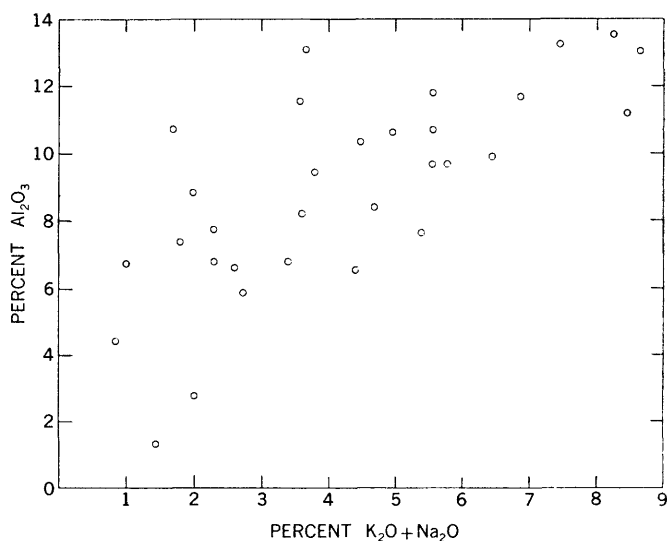


FIGURE 4.—Content of alkalis versus  $Al_2O_3$  of arkoses. Inasmuch as the bulk of the alkalis and alumina is present in feldspars, these oxides show a good positive correlation.

rocks. The sandy detrital material is embedded in a paste which has the composition of a slate. As a result, the content of both major and minor elements—including trace elements—is intermediate between that of normal sandstones and shales.

Graywackes are found throughout the geologic column. They are common in many Precambrian eugeosynclinal tracts. These (analyses B and D of table 7) do not seem to differ in any essential way from younger graywackes except, perhaps, that they seem to be a little richer in iron and magnesium.

#### ARKOSES

As is true of other rocks, the bulk chemical composition of the arkoses is rather closely circumscribed by the definition of the class. If, as commonly stated, arkoses are sands with 25 percent or more of feldspar, they will of necessity contain considerable  $Al_2O_3$  and be rich in the alkalis, notably  $K_2O$ . Thirty-five percent orthoclase would contribute 5.9 percent  $K_2O$  and 6.5 percent  $Al_2O_3$  and a rock with this much feldspar, assuming the balance (65 percent) to be quartz, would contain 87.6 percent  $SiO_2$ . (See fig. 4.)

The feldspar content of the rocks which have been classed as arkose ranges from less than 20 percent to more than 60 percent, and as can be seen from the analyses given (table 8), the silica (70-85 percent), alumina (7-14 percent), and  $K_2O$  (3-6 percent) approach the expected values. If the feldspar is somewhat sodic, or if some plagioclase is present, then  $Na_2O$  also becomes an important constituent of the rock. Lime is a major component only if the arkose is cemented by calcite. Iron oxide, generally ferric oxide, is present in part at least as a cement. In these sandstones,



TABLE 8.—Chemical analyses of arkose and subarkose

	A	B	C	D	E	F	G	H	I	J
SiO <sub>2</sub> .....	79.30	75.80	80.89	73.32	59.24	69.94	92.13	87.02	85.74	72.21
Al <sub>2</sub> O <sub>3</sub> .....	9.94	11.74	7.57	11.31	6.65	13.15	4.42	2.86	16.84	10.69
Fe <sub>2</sub> O <sub>3</sub> .....	1.00	.59	2.90	3.54	2.02		.37	.49	5.70	.80
FeO.....	.72	1.31	1.30	.72	.31		.33	.28		.72
MgO.....	.56	.54	.04	.24	.12	Trace	.14	.20	1.11	1.47
CaO.....	.38	1.41	.04	.75	16.04	3.09	1.27	3.41	.49	3.85
Na <sub>2</sub> O.....	2.21	2.40	.63	2.34	.19	5.43	.11	.00	1.16	2.30
K <sub>2</sub> O.....	4.32	4.51	4.75	6.16	2.30	3.30	.72	1.98	2.19	3.32
H <sub>2</sub> O+.....	.55	.86			1.26					1.46
H <sub>2</sub> O-.....	.41	.03	1.11	.30						.08
TiO <sub>2</sub> .....	.22	.15	.40						3.38	.22
P <sub>2</sub> O <sub>5</sub> .....	.05	.60							.01	.10
MnO.....	.02	.05			.50	.70	.24			.22
CO <sub>2</sub> .....		Trace		.92	12.16		None			2.66
Ignition loss.....						1.01	.42	3.35	1.12	
Total.....	99.68	99.99	99.63	99.60	100.79	99.10	100.15	99.65	99.83	100.10

<sup>1</sup> Contains MnO<sub>2</sub>.<sup>2</sup> Total iron.<sup>3</sup> Contains ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>.<sup>4</sup> Reported as MnO<sub>2</sub>.<sup>5</sup> Includes 0.06 percent S.<sup>6</sup> Sum given in original as 99.90.

- A. Jotnian (Precambrian), Kõyliö, Muurumäki, Finland. H. B. Wilk, analyst. Simonen and Kouvo (1955, p. 63). 44 percent normative feldspar.
- B. Torridonian (Precambrian), Kinlock, Skye, M. H. Kerr, analyst. Kennedy (1951, p. 258). 53 percent normative feldspar.
- C. Sparagmite (Lower Cambrian), Engerdalen, Norway. Barth (1938, p. 58). 33.5 percent normative feldspar.
- D. Lower Old Red Sandstone (Devonian), Foyers, Loch Ness, Scotland. Mackie (1899, p. 58). 52 percent normative feldspar.
- E. Calcareous arkose (Old Red Sandstone, Devonian), Red Craggs, Fochabers-on-Spey, Scotland, Mackie (1899, p. 58). 16 percent normative feldspar and 28 percent normative calcite.
- F. Portland Stone (Newark Group, Triassic), Portland, Conn. Merrill, (1891, p. 420). 74 percent normative feldspar.
- G. Subarkose, Rosebrae Sandstone (Devonian), Rosebrae, Elgin, Scotland. Mackie (1899, p. 58). About 12 percent normative feldspar.
- H. Calcareous subarkose, Cambrian or Ordovician, Bastard Township, Ontario, Canada. Keith (1949, p. 21). About 12 percent feldspar and 7 percent calcite.
- I. Subarkose of Whitehorse Group, Permian, Kansas, Swineford (1955, p. 122).
- J. Molasse Arkose, Oligocene (Zugertypus), Unterägeri, Kt. Zug, Switzerland, F. de Quervain, analyst. Niggli and others (1930, p. 262).

unlike the graywackes, the ferrous iron, magnesia, and water are low, and also, unlike the graywackes, K<sub>2</sub>O generally greatly exceeds Na<sub>2</sub>O, reflecting the greater importance of detrital orthoclase or microcline and the unimportance of albitic plagioclase in the arkoses.

## SPECIAL TYPES OF SANDSTONES

Few sandstones are chemically aberrant and do not belong to one of the common major classes. These are in part rocks transitional into other sediments—commonly chemical sediments. Included here are the greensands or glauconite-bearing sands, the sands cemented by or rich in phosphate, the siderite-, barite-, and anhydrite-cemented sands. Here also might be considered the sands impregnated with bitumen.

The glauconitic sands are represented by three analyses (A, B, and C) in table 9. As can be seen, they are characterized by their high total-iron content, principally ferric oxide, and by their high content of K<sub>2</sub>O. Quite commonly also, as shown by the New Jersey greensands, they are high in phosphorus. As would be expected, they also contain a good deal of combined water. Some greensands are high enough in iron to be classed as an iron-bearing formation or iron-stone.

Phosphatic sandstone is sand cemented with calcium phosphate (carbonate fluorapatite) or sandstone that

contains an appreciable quantity of phosphatic debris or precipitated granules or oolites of phosphate.

Ferruginous sands are heavily cemented by iron oxide that may be an oxidation product of siderite or that may have formed in some other manner. The writer was unable to find any analyses of sideritic sandstone, though sandstones with siderite or a mixture of siderite and calcite are not rare. An analysis of a ferruginous sandstone is included in table 9.

Barite, gypsum, and anhydrite are local cementing agents in some sandstones. The composition of barite nodules has been published elsewhere (Nichols, 1906; Ham and Merritt, 1944, p. 32).

## MINOR ELEMENTS IN SANDSTONES

Little systematic work has been reported on the minor elements of sandstones, although much work has been done on the minor accessory minerals ("heavy minerals") of these rocks.

Inasmuch as the major elements show wide ranges in abundance, one might expect similar wide variations in abundance of the minor elements. Some minor elements, such as zirconium and boron, are present in the minor accessory minerals such as zircon and tourmaline. Because some of these minerals are exceedingly stable, like the two just cited, one might expect enrichment of sands in certain minor elements relative to the plutonic source rocks from which the sands were derived. Other minor elements, such as barium, which substitute in less stable minerals, such as the feldspars, might be expected to be less abundant in the sandstones than in the source rocks.

TABLE 9.—Chemical analyses of miscellaneous sandstones

	A	B	C	D	E	F
SiO <sub>2</sub> .....	57.40	50.74	75.95	45.43	48.85	49.81
Al <sub>2</sub> O <sub>3</sub> .....	6.89	1.93	2.91	.03	11.82	5.17
Fe <sub>2</sub> O <sub>3</sub> .....	11.98	17.36	10.29	2.92	1.83	29.17
FeO.....	3.04	3.34			1.22	.35
MgO.....	2.41	3.76	1.37	.61	.45	.95
CaO.....	1.78	2.86	.10	26.21	12.85	2.43
Na <sub>2</sub> O.....	1.11	1.53	.35	.34	.47	.84
K <sub>2</sub> O.....	4.85	6.68	2.99	.16	.64	.48
H <sub>2</sub> O+.....	5.36	9.08	5.40	2.78	2.75	6.56
H <sub>2</sub> O-.....	4.46					3.85
TiO <sub>2</sub> .....	.29		.20	.11	Trace	
P <sub>2</sub> O <sub>5</sub> .....	.22	1.79		16.05	10.70	.42
CO <sub>2</sub> .....		.88		3.12	3.40	
MnO.....	.03			.02		
SO <sub>3</sub> .....	.45			.86		
F.....				1.87	2.86	
Total.....	1100.29	99.95	99.56	101.25	97.84	100.03
Less O.....				.79	1.20	
Total.....				100.46	96.64	

(1) Includes BaO, 0.02. (2) Includes C, 0.45. FeS<sub>2</sub>, 0.29. (3) Given as 99.01 in original.

- A. Greensand, Middle Eocene, Pahi Peninsula, New Zealand. Ferrar (1934, p. 47).
- B. Greensand marl, Upper Cretaceous, New Jersey, R. K. Bailey, analyst. Mansfield (1922, p. 124).
- C. Greensand, opal-cemented. Thanetien, Angre, Belgium. Cayeux (1929, p. 130).
- D. Phosphate sandstone, "Upper phosphorite stratum," Cenomanian, Kursk, Shchigri, U.S.S.R. Bushinsky (1935, p. 90). About 38 percent quartz, 45 percent phosphorite, 5 percent glauconite.
- E. Phosphatic sandstone, Saint Pôt, Boulonnais, France. Cayeux (1929, p. 191).
- F. Ferruginous sandstone, "carstone" from Hunstanton, Norfolk, England, Phillips (1881, p. 13). Consists of quartz grains cemented by brown iron ore, with a very little feldspar and mica.



The distribution of trace elements in sandstone is determined by the mineralogic composition of the detrital fraction and the nature and volume of the void-filling materials. The pure quartz sandstones devoid of cement carry trace elements characteristic of the quartz of which they are made. Presumably igneous and metamorphic quartz would be somewhat unlike in their trace-element content. Feldspars add considerable barium, but little strontium. Carbonate cement contributes magnesium, manganese, strontium, and barium, the strontium being derived from the aragonitic skeletal materials. Clay matrix—and argillaceous rock particles—add considerable quantities of such elements as boron, barium, cobalt, chromium, copper, gallium, nickel, titanium, and vanadium. The minor accessory detrital minerals (heavy minerals) are rich in zirconium, barium, cobalt, chromium, copper, nickel, scandium, titanium, vanadium, and silver. The greatest concentrations of some of these elements are in "black sands" or "placers" greatly enriched in heavy minerals. These natural concentrates are mined and constitute a source of such elements as titanium, thorium, zirconium, cerium, gold, tin, and tungsten.

*Titanium.*—As can be seen in table 1, titania appears to be correlated with the content of alumina and increases as grain size decreases. The titanium content of sandstones with large quantities of aluminous materials—argillitic rock particles and interstitial clay—is, therefore, higher than that of the more quartz-rich sandstones. Average graywacke (61 analyses), for example, contains 0.63 percent  $\text{TiO}_2$ ; the average lithic sandstone (11 analyses) and the average arkose (31 analyses) contain 0.24 and 0.27 percent  $\text{TiO}_2$ , respectively. Orthoquartzites have less than 0.15 percent titania. The average sandstones (weighted average of the above figures) would have about 0.24 percent  $\text{TiO}_2$  or about 1,440 ppm Ti. This is about half the value given by Vinogradov and Ronov (1956) for the sandstones of the Russian platform, but it is about the same as that of Clarke's (1924, p. 34) composite sample of 253 sandstones (see table 13, D and E). It is, however, higher than the 580 ppm Ti of a composite of 289 samples of 24 Paleozoic formations of the Colorado Plateau (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31)<sup>3</sup>.

*Phosphorus.*—The  $\text{P}_2\text{O}_5$  content of sandstones varies widely. It is generally a minor constituent but in exceptional rocks it may be a major component (table 9). It occurs mainly as phosphatic shell debris and probably to a lesser extent as detrital apatite and probably also replaces silicon in silicate minerals.

Koritnig (1951) reports a  $\text{P}_2\text{O}_5$  content in various German sandstones, quartzites, and graywackes ranging from 0.020 to 0.094 percent, corresponding to about 90 to 410 ppm P. Samples of four sandstones from Japan (Ikeda, 1952) average 0.089 percent  $\text{P}_2\text{O}_5$ . Clarke's composite of 253 sandstones contained 0.08 percent  $\text{P}_2\text{O}_5$ . Stokes' composite of 371 sandstones (Clarke, 1904, p. 20) used for building purposes contained 0.06 percent  $\text{P}_2\text{O}_5$ .

The average  $\text{P}_2\text{O}_5$  content of 61 graywackes (table 7) is 0.16 percent; that of 12 arkoses is 0.15 percent, and that of 14 lithic sandstones is 0.14 percent. The  $\text{P}_2\text{O}_5$  content of most orthoquartzites is nil. The weighted average of the above figures is about 0.10 percent  $\text{P}_2\text{O}_5$ . The phosphorus content of sandstones is thus about 90 to 700 ppm and averages about 400 ppm. Green (1959) gives the mean content in sandstones as 350 ppm P.

*Manganese.*—The manganese content of sandstones of Paleozoic and Mesozoic age of the Colorado Plateau (289 samples of 24 formations) is 140 ppm Mn, equivalent to about 0.018 percent MnO (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31).

The average MnO content of 37 graywackes is 0.11 percent. This is about 775 ppm Mn, a figure of the same order of magnitude as the manganese content of shale and phyllite and the average igneous rock (Rankama and Sahama, 1950, p. 652). The average of 16 Precambrian "arkosic and feldspathic" graywackes is 579 ppm Mn (Macpherson, 1958). The high silica orthoquartzites would probably be poorer in manganese content. Ronov and Ermishkina (1959) give the average MnO content of Russian sandstones (410 analyses) as 0.063 percent which corresponds to about 487 ppm Mn. According to these authors, the greatest concentration of manganese occurs in the near-shore marine facies.

*Zirconium.*—Zirconium is probably present in most sandstones in the ubiquitous detrital zircon. In the mature orthoquartzitic sands, zircon (and perhaps tourmaline) are the only surviving heavy minerals. The zirconium content of sands is seldom reported. Some data are available, however, on the zirconium content of glass sands. Poole and Segrove (1957) give the  $\text{ZrO}_2$  content of English glass sands as 0.005 to 0.014 percent. Indiana glass sands (Murray and Patton, 1953) range from 0.01 to 0.11 percent  $\text{ZrO}_2$ . The St. Peter sandstone (Ordovician) contains 0.02 percent; composite samples of the Cypress Sandstone (Mississippian) contain 0.04, 0.08, and 0.11 percent  $\text{ZrO}_2$ . Composite samples of sandstone of the Mansfield formation (Pennsylvanian) contain 0.06, 0.07, and 0.04 percent  $\text{ZrO}_2$ . The zirconium content of Indiana glass sands, therefore, ranges from 74 to 820

<sup>3</sup> These authors give only geometric means, which are generally lower than the arithmetic means.

ppm and is appreciably higher than that of the English glass sands which range from about 37 to 100 ppm.

Franciscan graywacke (Taliaferro, 1943, p. 136) contains 0.05 percent  $ZrO_2$  (370 ppm Zr) and a lower Mesozoic graywacke from New Zealand (Speight, 1928, p. 408) contains 0.03 percent  $ZrO_2$  (220 ppm Zr).

The zirconium content of a composite sample of Paleozoic and Mesozoic sandstones of the Colorado Plateau (289 samples from 24 formations) was 88 ppm, which is equivalent to about 0.01 percent  $ZrO_2$  (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31). Degenhardt (1957, p. 302) gives analyses of many sandstones for zirconium. These range from 33 to 480 ppm and average about 220 ppm, which is equivalent to about 0.02 percent  $ZrO_2$ . The quartzites are the richest in zirconium; some contain as high as 770 ppm (0.10 percent  $ZrO_2$ ) (von Engelhardt, 1936, p. 187).

**Sulfur.**—Sulfur is contained in sandstones as iron sulfide, generally pyrite, and as sulfates of calcium (anhydrite and gypsum), and, more rarely, as barium sulfate (barite). The sulfide is almost certainly diagenetic or introduced. The sulfates are generally a component of the cement. Rarely are they a major component.

Vinogradov and Ronov (1956) report a mean of 0.69 percent  $SO_3$  in the sandstones of the Russian platform. Clarke's composite of 253 sandstones, however, contained only 0.07 percent  $SO_3$  (Clarke, 1924, p. 30). Graywackes (table 7) average 0.25 percent  $SO_3$  and 0.07 percent sulfide sulfur. This corresponds to 1,700 ppm of S.

**Barium and strontium.**—The average BaO content of 18 feldspathic graywackes is 0.05 percent, which corresponds to about 450 ppm Ba. The average of 16 Precambrian "arkosic and feldspathic" graywackes is 360 ppm Ba (Macpherson, 1958). The composite sample of 253 sandstones analyzed by Stokes (Clarke, 1924, p. 547) contains the same proportion of barium. No doubt the feldspar-poor orthoquartzites would be appreciably lower in barium content, except in those sandstones with detrital or authigenic barite.

The barium content (geometric mean) of Paleozoic and Mesozoic sandstones of the Colorado Plateau (289 samples of 24 formations) is 280 ppm, equivalent to about 0.03 percent BaO (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31). Von Engelhardt (1936, p. 187) estimates the barium content of sandstones to be 170 ppm. In view of the above figures, this value seems too low.

Inasmuch as the SrO content of the silicic plutonic rocks is generally lower than that of BaO, very probably the SrO content of sands would likewise be lower. The meager data available seem to support this conclusion. The strontium content of sandstones of the

Colorado Plateau (composite of 289 samples of 24 Paleozoic formations) is given as 45 ppm (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31. Noll (1934, p. 507) estimated the Sr content of sandstones to be 26 ppm.

**Summary.**—The elements discussed above have been sought for and found in composite samples large enough or determined with sufficient regularity in ordinary analyses that some valid conclusions can be drawn concerning their abundance in sandstones. These are summarized in table 10. The "averages" tabulated are approximations only and constitute a judgment based on the data available.

#### TRACE ELEMENTS IN SANDSTONES

In addition to the minor elements summarized in table 10, other elements are present in only a few parts per million. These might be collectively called trace elements. In general, the data on the distribution of the trace elements in sandstones are not very good. Very few analyses have been made on composite samples, properly made up, or even on selected samples which are properly described and identified. As a result, no good average value can be given for many of these elements. One can sometimes make better estimates of abundance of an element in sandstone based on its known geochemical behavior than one can secure by simply averaging the concentrations found by a few sporadic or poorly documented analyses.

The ore metals copper, zinc, lead, gold, silver, cobalt, and nickel are very rare in sands despite the fact that some of these and other metallic elements (such as gold, platinum, and tungsten) are won from placer sands.

TABLE 10.—Minor and trace elements of sandstones <sup>1 2</sup>

[Values in ppm or grams per ton]

Element <sup>3</sup>	Ranges reported in both composite and single samples	Approximate average	Element <sup>3</sup>	Ranges reported in both composite and single samples	Approximate average
Ti.....	580-3,480	1,500	Be.....	.....	2
P.....	90-700	350-450	Y.....	.....	4
Mn.....	140-775	500	Ge.....	.....	1-2
Zr.....	37-820	200-250	Ga.....	.....	5-10
S.....	280-2,760	2,000	Cu.....	.....	10-20
Ba.....	170-450	300	Zn.....	.....	16
Sr.....	26-45	35	Pb.....	.....	9
F.....	.....	200	Ni.....	.....	2
Cl.....	.....	10	V.....	.....	10-20
B.....	.....	20-30	Cr.....	.....	10-20
Li.....	.....	15	W.....	.....	1-2
Rb.....	.....	60	Th.....	.....	1-2

<sup>1</sup> Turekian and Wedepohl (1961) gives values (in parts per million) of 170 for P, 30 for Mn, 240 for S, and 30 for Ba. They also report 0.X for Be, 40 for Y, X.0 for Cu, 1.7 for I, and 30 for La. These values differ significantly from those compiled by the author.

<sup>2</sup> Turekian and Wedepohl (1961) have also estimated the concentration (ppm) in sandstones of As as 1, Se as 0.05, Nb as 0.0X, Mo as 0.2, Ag as 0.0X, Cd as 0.0X, In as 0.0X, Sn as 0.X, Sb as 0.0X, Ce as 92, Pr as 8.8, Nd as 37, Ba as 10, Eu as 1.6, Gd as 10, Tb as 1.6, Dy as 7.2, Ho as 2.0, Er as 4.0, Tm as 0.3, Yb as 4.0, Lu as 1.2, Hf as 3.9, Ta as 0.0X, Au as 0.00X, and Hg as 0.03.

<sup>3</sup> Present, 1 ppm or <1 ppm: Br, I, Cs, La, Sc, Ti, In, Co, U.

The data, although incomplete and inadequate, are summarized in the following section. Compare also the data in table 14.

*Fluorine, chlorine, bromine, and iodine.*—Of the halogens, fluorine and chlorine are the most important. They are contained in detrital apatite, in phosphatic skeletal debris, and in precipitated "collophane." The average sandstone contains about 350 ppm P and, if this were contained in fluorapatite, about 100 ppm of fluorine should be present. However, fluorine may also be present in the clay minerals.

Koritnig (1951) reports 0.045 percent F in 11 Carboniferous sandstones, 0.032 percent in 23 samples of Bundsandstein, 0.028 percent in 11 Cretaceous sandstones. Ten quartzites had 0.020 percent, and 17 graywackes contained but 0.004 percent. This corresponds to a range of 40 to 450 ppm and an average of 270 ppm of fluorine. Kokubu (1956) gives the fluorine content of sandstones as 290 ppm. A collection, made by Michael Fleischer (written communication, 1960) of analyses of 49 sandstones and graywackes, showed 10 to 880, average 180 ppm F.

Chlorine is also a constituent of some phosphatic materials. It is also present in the interstitial brines of many sediments and sedimentary rocks. Except in sandstones containing brines, chlorine is not as abundant as fluorine. Behne (1953) states that sandstones contain 10 ppm Cl. The Tanner graywacke contains 20-70 ppm; other graywacke was still richer in Cl.

Bromine and iodine occur in even smaller quantities. Bromine is present in 1 ppm or less (Behne, 1953); graywackes contain 3 to 12 ppm Br. Iodine is present in lesser concentrations.

*Boron.*—Boron is a constituent of tourmaline, a common heavy mineral in many sandstones. It is generally detrital, but authigenic overgrowths are also known.

Boron is seldom determined in sandstones. A glauconitic sandstone contained 155 ppm boron (Goldschmidt and Peters, 1932). This is exceptionally high, inasmuch as quartzites from southern Lapland contain 9 to 31 ppm (Sahama, 1945) and those of Eocambrian age (Ström quartzites) contain 0.013 to 0.054 percent and average 0.022 percent  $B_2O_3$  (equivalent to about 68 ppm B) (Landergrén, 1945). If the boron of the St. Peter sandstone (Ordovician) is contained wholly in detrital tourmaline, the concentration of boron probably would not exceed 10 ppm, inasmuch as tourmaline rarely forms more than half the heavy-mineral fraction which itself makes up less than 0.05 percent of the sand (Thiel, 1935). The boron content of 289 samples of 24 sandstones of Paleozoic and Mesozoic age of the Colorado Plateau is 16 ppm (Shoemaker, Miesch,

Newman, and Riley, 1959, p. 31). Harder (1959) estimates the boron content of sandstones to be 35 ppm.

In view of the above observations the value of 155 ppm for the boron content of sandstones shown on Green's chart (1959) is probably much too high. The true value is nearer one fifth this figure. As the boron content of shales is notably greater, those sandstones rich in pelitic materials, either matrix or rock particles, might be richer in boron. This conclusion is supported by the Tanner graywacke (Helmbold, 1952) the fine, medium, and coarse specimens of which contain 37, 28, and 18 ppm B respectively. Macpherson (1958) reports 44 ppm B in 16 Precambrian "arkosic and feldspathic graywackes." A reasonable estimate for the average sandstone, therefore, is 25-35 ppm B. Glauconitic sandstones are notably enriched in boron.

*Lithium, rubidium, and cesium.*—Lithium is largely retained in the products of weathering and is concentrated in clay minerals (Horstman, 1957). The lithium content of sandstones will vary with the source of the quartz and with the clay impurities. Horstman gives 15 ppm as the average content of lithium in sandstones. This is in good agreement with Strock (1936). Horstman's conclusion, however, is apparently based on only four sandstones, one of which was glauconitic and richer in lithium (25 ppm). Inasmuch as shales are appreciably richer in lithium than are sandstones, the sandstones containing argillitic rock particles or a considerable quantity of clay in the matrix, such as the graywackes, should contain more lithium than the high-quartz sands.

Rubidium apparently substitutes for potassium and hence would be expected to be more abundant in the feldspathic sands. As rubidium does not enter the quartz structure (Horstman, 1957), pure quartz sands will be low in rubidium. Arkoses and feldspathic graywackes might be expected to contain more rubidium; and as shales are potassic and hence richer in rubidium, the sandstones with argillitic detritus or matrix should be richer in rubidium. Horstman's analyses of four sandstones show a range from 20 to 100 ppm. The highest value was found in a glauconitic sand. Horstman's average is 60 ppm Rb for sandstone.

Although shales contain measurable amounts of cesium, the sandstones, excepting the glauconitic sandstone (9 ppm Cs), contained no detectable cesium.

*Beryllium.*—Beryl is the principal mineral that contains beryllium and as it is a durable mineral it might be expected to occur as a detrital mineral in some sandstones. Pieruccini (1943) found 3 to 7 ppm BeO in eight sandstones from Italy (average 4.5 ppm BeO or 2 ppm Be). No detectable BeO (less than 10 ppm) was found in most of the sandstones investigated by

Warner and others (1959, p. 26); BeO was found in three sandstones (4, 40, and 70 ppm). Sandstones, therefore, contain on the average about 2 ppm Be and exceptionally may contain as much as 25 ppm of this element.

*Rare earth elements and scandium.*—Data on the occurrence of the rare earth elements in sandstones are exceedingly rare. Rankama and Sahama (1950, p. 508), in a review of the literature give as averages for sandstones, 0.7 ppm Sc and 1.6 ppm Y. Quartzite from southern Lapland is reported to contain 17 ppm La and 24 ppm Ce (Sahama, 1945). Little is known about their occurrence in sandstones. The unmineralized Upper Triassic sandstones (Chinle Formation) of the Colorado Plateau are estimated to contain 4 ppm Sc, 16 ppm Y, and 8 ppm La. The average sandstones of the Colorado Plateau (289 samples of 24 formations) contain 4 ppm Y (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31). Data on phosphorites suggest that phosphatic sandstones would be enriched in rare earths.

*Gallium and germanium.*—Meager data (Burton, Culkin, and Riley, 1959) suggest that sandstones contain 1–2 ppm Ge and 1–15 ppm Ga. The gallium content is higher in the more aluminous sandstones, such as the graywackes. Gallium exceeds germanium in most sandstones; 1–2 ppm Ge and 5–10 ppm Ga are values of the right order of magnitude.

*Thallium and indium.*—Thallium occurs only in trace amounts in sandstones. Preuss (1941) reports 2 ppm Tl as an average for sandstones. This figure is appreciably higher than those reported by Shaw (1952a). In three graywackes Shaw found that thallium did not exceed 0.3 ppm and only in an arkose did it reach 1.3 ppm. The average thallium content of sandstone, therefore, is probably less than 1 ppm.

Indium was not found in ordinary sandstones and was present in only a fraction of one part per million in graywackes (Shaw, 1952b).

*Copper.*—Carobbi and Pieruccini (1943) report copper in concentration ranging from 8 to 15 ppm in eight sandstones; Itkina (1946) gives an average of 18 ppm Cu in 30 sandstones. Strakhov and others (1944) report three analyses of sandstones which contained none, 20, and 400 ppm Cu. The average copper content of all sandstones in the Colorado Plateau (289 samples of 24 formations, Cambrian to Cretaceous) is 9 ppm (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31). Katchenkov (1959) reports values ranging from "trace" to 35 ppm and an average of 19 ppm. Weber (1960) reported 9 to 37 ppm Cu for graywackes (mainly Ordovician) from eastern Canada and New York State. Macpherson (1958), however, reports an average of 46 ppm Cu in 16 "arkosic and feld-

spathic graywackes" of Precambrian age in Ontario. Macpherson's graywackes, as a class, are richer in copper than other sandstones—perhaps because they come mainly from a mineralized province. It is probable that the copper content of the average sandstone is somewhere between 10 and 20 ppm.

*Lead and zinc.*—The lead content of ordinary sandstones has been estimated, from a study of German sandstones and quartzites, to be 7–8 ppm (Wedepohl, 1956). Some arkoses and red sandstones were found to be notably richer in lead. The same sandstones and quartzites contain on the average 16 ppm Zn; German graywackes contain 61 ppm Zn (Wedepohl, 1953).

*Cobalt and nickel.*—Cobalt and nickel have been reported in small quantities in some sandstones. Sandstones of the Colorado Plateau (289 samples of 24 formations, Cambrian to Cretaceous in age) contain 1 ppm Co and 2 ppm Ni (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31). These values are virtually the same as reported by Lundegårdh (1949) for the sandstone of Västergötland, Sweden. Sahama (1945) found 2 to 8 ppm Ni in the quartzites of southern Lapland. Macpherson (1958) found 90 ppm Ni in Precambrian graywackes of Ontario. The high value is perhaps related to the argillaceous debris and matrix of these sandstones.

Heavy metals rarely found in sandstones or present in less than 1 ppm include molybdenum (Kuroda and Sandell, 1954), mercury, bismuth, silver, and gold (Krauskopf, 1955).

*Vanadium.*—Vanadium is present in many sandstones. As it is generally incorporated and concentrated in hydrolyzates and oxides, sandstones rich in argillaceous or ferruginous matter are richer in vanadium.

Early work by Jost (1932) has shown sandstones to contain on the average 20 ppm V. The concentrations determined ranged from less than 5 ppm to 86 ppm. Hillebrand (1900) reports 0.003 percent  $V_2O_5$  (17 ppm V) in a composite sample of 253 sandstones. The unmineralized sandstones of the Colorado Plateau, Cambrian to Cretaceous in age (24 formations of 289 samples), contain 11 ppm V (Shoemaker and others, 1959, p. 31). The Salt Wash Member of the Morrison Formation (Jurassic) contains 10 ppm (96 samples). The vanadium content of bitumen-free sandstones in the Urals and the near-Volga area is 73 ppm, according to Romm (1946). Krauskopf's estimate (1955) of 10 to 60 ppm V for sandstones is the right order of magnitude. The average sandstone probably contains nearer 10 to 20 ppm.

*Chromium.*—Chromium, reported as  $Cr_2O_3$ , is present in small quantities in some sandstones. The quartz-

ites of southern Lapland are said to contain 68 to 200 ppm Cr (Sahama, 1945). These values seem high inasmuch as a weighted mean of 7 ppm is reported in 289 samples of 24 formations, Paleozoic and Mesozoic in age, in the Colorado Plateau (Shoemaker, Miesch, Newman, and Riley, 1959, p. 31). The geometric mean of 96 samples of the Salt Wash Member of the Morrison Formation (Jurassic) was 6.6 ppm. Von Engelhardt (1936) in a study of sandstones in Germany reports averages of 48 ppm in Karbonsandsteinen, 20 ppm in Buntsandsteinen, and 150 ppm in quartzites. Lunde-gardh (1949, p. 51) reports 5 to 6 ppm in glacial sands of Sweden and less than 1 ppm from Cambrian sandstones. On the other hand, 16 Precambrian graywackes contained 196 ppm Cr (Macpherson, 1958). Frölich (1960) reports 1 to 123 ppm Cr in German sandstones. He estimates the average to be 58 ppm. Krauskopf's estimate (1955, p. 416) of 10 to 100 ppm Cr in sandstones is probably about right although, with a few exceptions, the correct value must be nearer 10 rather than 100.

Chromium in sandstone is probably in the form of the mineral chromite (Rankama and Sahama, 1950, p. 623) and also in the clay components (Frölich, 1960).

*Tungsten.*—Tungsten is present in small quantities in sandstones. Vinogradov and others (1958) report 1.6 ppm W in sandstones. Jeffery (1959) found 1 ppm or less to 34 ppm in sandstones and quartzites of Uganda. The average fell in the 2 to 5 ppm range but inasmuch as some of the samples came from an area of tungsten mineralization, the values obtained may be too high. A more reasonable figure is 1 to 2 ppm.

*Thorium and uranium.*—Except for some rare placer sands, thorium and uranium are present in very small quantities in sands and sandstones. Murray and Adams (1958, p. 263) found an average between 1 and 2 ppm of thorium and about 0.5 ppm of uranium in present-day sands of Galveston Island, Tex. The St. Peter Sandstone (Ordovician) and similar high-purity sandstones contain a little less; the Berea Sandstone (a Mississippian protoquartzite) contains about twice as much as the modern beach sands.

Several placer sands, rich in zircon and monazite, have high concentrations of both thorium and uranium. A Florida beach sand, for example, has 160 ppm Th and 75 ppm U.

#### ORGANIC-CARBON CONTENT OF SANDSTONES

As is well known, the content of organic matter, and hence organic carbon, varies inversely as the grain size of clastic sediments. Hence, as might be expected, the content of organic matter in sandstones is generally low and much lower than in the associated shales. Except for those rare sandstones in which bituminous

or asphaltic matter has been introduced, organic carbon is a minor element in the composition of sandstones. The "coal measure sandstones" are perhaps a further exception, with abundant plant fragments—essentially mineral charcoal or fusain.

The most extensive investigation of the subject is that of Ronov (1958), who states that the sandstones of the Russian platform contain, on the average, 0.24 percent organic carbon. This estimate was based on 402 composite samples. Marine sands were found to contain on the average 0.33 percent, more than twice as much organic carbon as is found in continental and lagoonal sands (0.15 percent).

#### THE AVERAGE SANDSTONE

It is perhaps of interest to know what the chemical composition of the "average sandstone" is.

The published analyses, even good ones, are not necessarily representative of sandstones. They are commonly made because the rock was of special economic interest as a source of silica or as a building stone, or because it was an unusual or rare type, perhaps glauconitic or phosphatic. It is unlikely, therefore, that the chemical composition of the "average sandstone" could be ascertained merely by averaging the available analyses, no matter how many nor how complete.

Clarke attempted to estimate the composition of the average sandstone by making one analysis of a composite sample of 253 sandstones. The makeup of the sample is unknown but it presumably was composed largely of sandstones from North America. No record is available of the stratigraphic and geographic coverage of the sample analyzed. The turbidite sandstones of thick flysch formations are likely to be underrepresented as they are neither mappable units nor of economic interest. A good deal of thought and skill is needed to prepare a representative composite sample.

Another approach to the problem is to compute averages for the common types of sandstones and then from estimates of the abundance of these types, compute the bulk composition of an average sandstone. This was in essence the method utilized by Middleton (1960). Several estimates of the abundance of the common types have been made (Krynine, 1948; Tallman, 1949; Pettijohn, 1957; Bokman, 1955). Because some disagreement exists on the defining parameters and their limits the several estimates are somewhat unlike (table 11). If, however, the sample from which the estimates and the averages of the several types were obtained (table 12) is valid, the computed bulk chemical composition should be acceptable.

The author has made no special effort to collect a representative sample of sandstone but has instead taken the collections available to him—at The Johns

TABLE 11.—Relative abundance of sandstone classes

Class	Krynine (1948) <sup>1</sup>	Pettijohn <sup>2</sup>	Middleton (1960) <sup>3</sup>	Tallman (1949) <sup>4</sup>
Orthoquartzite.....	22.5	34	34	45
Arkose <sup>5</sup> .....	32.5	15	16	17
Graywacke ("high-rank gray- wacke").....	10.0	26	24	17
Lithic arenite ("low-rank gray- wacke" or subgraywacke).....	35.0	20	26	21
Miscellaneous.....		5		

<sup>1</sup> Basis of estimate not stated.

<sup>2</sup> Pettijohn, F. J. New estimate (1960), based on 121 sandstones in Johns Hopkins collection for which thin sections are available. The Hopkins collection utilized in obtaining these estimates was obtained from 34 states and provinces and 7 foreign countries. The states and provinces provided samples as follows: Maryland and Texas, 12 each; Pennsylvania, 8; Wisconsin and New York, 7 each; California and Ontario, 6 each; Michigan and Wyoming, 5 each; Colorado, 4; North Carolina, Massachusetts and Nova Scotia, 3 each; Minnesota, Oklahoma, New Mexico, Kansas, Ohio, New Jersey, Louisiana, Tennessee, 2 each; Missouri, Arkansas, Washington, Montana, South Dakota, Connecticut, Virginia, Illinois, Alaska, Alberta, British Columbia, and Quebec, 1 each. Twenty-eight samples came from seven foreign countries, namely, Greenland, Germany, Scotland, Australia, Egypt, Mexico, and India. The samples have a wide stratigraphic range. Twenty-eight are Precambrian, 10 Cambrian, 11 Ordovician, 7 Silurian, 12 Devonian, 6 Mississippian, 12 Pennsylvanian, 2 Permian, 12 Triassic, 2 Jurassic, 13 Cretaceous, 19 Tertiary, and 4 other unknown. From point of view of time involved the Precambrian is under-represented; from point of view of area involved the Maryland-Pennsylvania area is oversampled (about 15 percent of total collection).

<sup>3</sup> Based on 167 sandstones for which chemical analyses appear in published literature.

<sup>4</sup> Based on sample of 275 sandstones, Cambrian to Tertiary in age, from all parts of United States.

<sup>5</sup> Includes subarkose.

TABLE 12.—Mean composition of principal sandstone classes

	Ortho- quartzite <sup>1</sup>	Lithic arenite <sup>2</sup>	Gray- wacke <sup>3</sup>	Arkose <sup>4</sup>
SiO <sub>2</sub> .....	95.4	66.1	66.7	77.1
Al <sub>2</sub> O <sub>3</sub> .....	1.1	8.1	13.5	8.7
Fe <sub>2</sub> O <sub>3</sub> .....	.4	3.8	1.6	1.5
FeO.....	.2	1.4	3.5	.7
MgO.....	.1	2.4	2.1	2.4
CaO.....	1.6	6.2	2.5	2.7
Na <sub>2</sub> O.....	.1	.9	2.9	1.5
K <sub>2</sub> O.....	.2	1.3	2.0	2.8
H <sub>2</sub> O+.....	.3	3.6	2.4	9
H <sub>2</sub> O.....		.7	.6	
TiO <sub>2</sub> .....	.2	.3	.6	.3
P <sub>2</sub> O <sub>5</sub> .....		.1	.2	.1
MnO.....		.1	.1	.2
CO <sub>2</sub> .....	1.1	5.0	1.2	3.0
SO <sub>2</sub> .....			.3	
S.....			.1	
BaO.....				
O.....			.1	
Total.....	100.7	100.0	100.4	100.0

<sup>1</sup> Computed from analyses published by Biggs and Lamar (1955, p. 18), Buttram (1913, p. 50), Cayeux (1929, p. 155), Collins (1925, p. 68), Cushing, Leverett, and Van Horn (1931, p. 110), Fetzke (1918, p. 164, 263), Van Hise and Leith (1911, p. 256-257), Moore and Taylor (1924, p. 29), Murray and Patton (1933, p. 28, 29), Rothrock (1944, p. 151), Simonen and Kuovo (1955, p. 79), Thiel (1935, p. 601), Weidman (1907, p. 45), and Keith (1949, p. 18, 19, 21). Total, 26 analyses.

<sup>2</sup> Computed from analyses published by Biggs and Lamar (1955, p. 18); Cayeux (1929, p. 161, 163, 176, 227; 9 analyses); Nanz (1954, p. 114); Niggli and others (1930, p. 51, 263); Phillips (1881, p. 21); Turner (1891, p. 396); and an analysis by V. C. Smith, of the U. S. Geological Survey. Total, 20 analyses.

<sup>3</sup> Based on analyses of 28 New Zealand graywackes (Paleozoic and Mesozoic) from Reed (1957, p. 16), 13 Precambrian graywackes from Diller (1890, p. 429, 1898, p. 84), Grout (1926, p. 19, 1933, p. 977), Horwood (1938, p. 24), James (1951), Macpherson (1958, p. 76), Pettijohn (1957, p. 306, 319), Todd (1928, p. 20), and Visser (1956, p. 63), and on 20 miscellaneous graywackes from Balk (1953, p. 824), Cayeux (1929, p. 171), Edwards (1950a, p. 139, 1950b, p. 169), Eigenfeld (1933, p. 58), Helmbold (1952, p. 256), and Taliaferro (1943, p. 136). Total, 61 analyses.

<sup>4</sup> Computed from analyses published by Barth (1938, p. 64), Cayeux (1929, p. 202, 209, 210, 212), Diller (1898, p. 77), Keith (1949, p. 21), Kennedy (1951, p. 258), Merrill (1891, p. 420), Mackie (1899, p. 58, 59; 13 analyses), Niggli and others (1930, p. 263), Simonen and Kuovo (1955, p. 63, 68), and Swineford (1955, p. 122). Total, 32 analyses.

<sup>5</sup> Estimated from CaO.

Hopkins University—containing some sandstones and has assigned these materials to the principal sandstone families or clans for which average chemical compositions have here been calculated. Weighting these averages properly, the mean chemical composition of sandstone has been computed. These results are shown

TABLE 13.—Chemical composition of the average sandstone

	A	B	C	D	E	F	G
SiO <sub>2</sub> .....	70.14	68.54	72.97	70.00	78.66	84.86	77.6
Al <sub>2</sub> O <sub>3</sub> .....	8.28	7.80	7.56	8.22	4.78	5.96	7.1
Fe <sub>2</sub> O <sub>3</sub> .....	12.41	13.03	12.91	12.52	1.08	1.39	1.7
FeO.....	1.51	1.77	1.99	1.51	.30	.84	1.5
MgO.....	2.03	1.29	1.60	1.89	1.17	.52	1.2
CaO.....	4.10	5.05	4.43	4.25	5.52	1.05	3.1
Na <sub>2</sub> O.....	.54	.81	.62	.58	.45	.76	1.2
K <sub>2</sub> O.....	2.09	1.93	2.05	2.06	1.32	1.16	1.3
H <sub>2</sub> O+.....					1.33	1.47	1.7
H <sub>2</sub> O.....					.31	.27	.4
TiO <sub>2</sub> .....	.60	.48	.46	.58	.25	.41	.4
P <sub>2</sub> O <sub>5</sub> .....					.08	.06	.1
MnO.....	1.07	1.06	1.04	1.06	Trace	Trace	.1
CO <sub>2</sub> .....	3.94	4.02	3.13	3.87	5.04	1.01	2.5
SO <sub>2</sub> .....	.78	.31	.23	.69	.07	.09	.1
Cl.....					Trace	Trace	Trace
F.....							Trace
S.....							Trace
BaO.....					.05	.01	Trace
SO.....					Trace	None	Trace
C.....				1.24			Trace
Ignition loss.....	2.91	3.70	2.98	3.02			
Total.....	99.40	98.79	99.97	99.49	100.41	99.86	100.0

<sup>1</sup> After Ronov and Ermishkina (1959): average of 410 analyses.

<sup>2</sup> Includes organic matter.

<sup>3</sup> After Ronov (1958): average of 402 analyses.

- A. Paleozoic sandstones of the Russian platform. Average of 130 analyses. Vinogradov and Ronov (1956).  
 B. Mesozoic sandstones of the Russian platform. Average of 23 analyses. Vinogradov and Ronov (1956).  
 C. Cenozoic sandstones of the Russian platform. Average of 5 analyses. Vinogradov and Ronov (1956).  
 D. Average sandstone of the Russian platform. Average of 158 analyses (3,709 samples). Vinogradov and Ronov (1956).  
 E. Average sandstone. Composite analysis of 253 sandstone. H. N. Stokes, analyst. Clarke (1904, p. 20).  
 F. Average sandstone used for building purposes. Composite of 371 sandstones. H. N. Stokes, analyst. Clarke (1904, p. 20).  
 G. Average sandstone computed by taking 26 parts average graywacke, 25 parts average lithic sandstone (subgraywacke), 15 parts average arkose, and 34 parts average orthoquartzite. New estimate, F. J. Pettijohn, 1960.

in table 13. Other averages have been included in this table for comparative purposes.

The author's average differs somewhat from that given by Clarke based on chemical analysis of a composite sample and, like Clarke's average, it differs materially from the average of the 345 analyses of sandstone used for building purposes. It resembles rather more closely the average given by Middleton, who arrived at his results in a somewhat similar manner and used most of the same analyses, and it resembles also the mean composition of the sandstones of the Russian platform, a mean obtained from 158 analyses of more than 3,000 samples (Vinogradov and Ronov, 1956). It lies in general between Clarke's composite and the average sandstone of the Russian platform. Compare also the data in table 14.

#### SECCULAR VARIATION IN CHEMICAL COMPOSITION

Although there is some evidence that feldspar content of sandstones increases with decreasing age, as do the number of heavy-mineral species (Pettijohn, 1957, p. 686), data are inadequate to demonstrate any important change in bulk chemical composition. However, the CaO/MgO ratio appears to increase with decreasing age. The data of Vinogradov and Ronov (1956) show ratios of 0.78 in pre-Devonian sandstones, 1.39 in the Devonian, 3.56 in the Carboniferous, and 3.90 in Meso-



zoic sandstones. This change is similar to that found in the carbonate rocks by Daly (1909) and may be related to progressive dolomitization of the carbonate cement with the passage of time. It could also be due to inclusion of more shelly materials in the younger sandstones (or to removal or silicification of such materials in the older rocks).

### GERMAN SANDSTONES

While this manuscript was in the final stages of preparation, K. H. Wedepohl of the University of Göttingen, Germany, sent chemical and spectrographic analyses of three composites of sandstones and of one composite of graywackes. These were received too late to be incorporated into the text. The analyses were made by many investigators over a period of nearly 30 years.

TABLE 14.—Analyses of German sandstone composite samples

[K. H. Wedepohl, written communication, August, 1961]

Major elements				
[In percent]				
	A	B	C	D
SiO <sub>2</sub> .....	66.7	79.25	80.95	89.9
Al <sub>2</sub> O <sub>3</sub> .....	1.83	.27	7.44	.23
FeO.....	3.86	3.39	1.49	3.0
MgO.....	3.09	.21	.69	.54
CaO.....	1.90	.89	.62	.064
Na <sub>2</sub> O.....	1.75	1.73	2.65	.37
K <sub>2</sub> O.....	2.65	1.55	2.01	.64
H <sub>2</sub> O+.....	.48	.23	.52	.15
H <sub>2</sub> O.....	.54	.24	.30	.083
TiO <sub>2</sub> .....	.094	.045	.076	.020
P <sub>2</sub> O <sub>5</sub> .....	.097	.072	.022	.014
MnO.....	2.40	1.34	1.3	1.51
CO <sub>2</sub> .....	.005	.012	.02	.024
SO <sub>3</sub> .....	.12	.014	.003	.004
S.....				
C.....				
Minor and trace elements				
[In ppm]				
Li.....	40	29	16	7
B.....	35	35	40	25
N.....	220	190	98	45
F.....	40	450	320	280
S.....	1,200	260	230	280
Cl.....	100			
Ti.....	3,200	1,400	1,700	500
V.....			19	
Cr.....		68	20	
Mn.....	*750	*560	*170	*110
Ni.....	*40	*27	*22	*14
Cu.....	*32	*39	33	*37
Zn.....	61	41	16	12
Ge.....	*46	*58	*17	*17
	1.4		.9	
Rb.....	*51	*52	*85	*≤10
Sr.....	*120	*88	*78	*21
Zr.....	*300	140	370	200
Ba.....	290	430	810	67
	*260	*270	620	*≈50
Pb.....			31	5
In.....			.3	
Sb.....			1	
Hg.....			.1	
Tl.....			2	
Bi.....			.3	
Mineral composition				
[Estimated]				
Quartz.....	30	57	65	80
Feldspar.....	40	10-15	20-25	3-5
Chlorite.....	10	≈5		
Micas (illite).....	10	≈3	5-8	≤3
Carbonates.....	6	3	3	3

### EXPLANATORY NOTES

- A. Composite of 17 graywackes  
 B. Composite of 11 Karbonsandsteine (sample prepared by von Engelhardt, 1934)  
 C. Composite of 23 Buntsandsteine (sample prepared by von Engelhardt)  
 D. Composite of 12 Kreidesandsteine (sample prepared by von Engelhardt, 1934)  
 \*Unpublished spectrographic determinations by Wedepohl.

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