Data of Geochemistry

Sixth Edition

Chapter T. Nondetrital Siliceous Sediments

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Michael Fleischer, *Technical Editor*

Chapter T. Nondetrital Siliceous Sediments

By EARLE R. CRESSMAN

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Tabulation and discussion of chemical
analyses of chert with respect to
mineralogic composition, petrographic
type, and geologic occurrence

UNITED STATES DEPARTMENT OF THE INTERIOR

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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 type.

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DATA OF GEOCHEMISTRY

NONDETRITAL SILICEOUS SEDIMENTS

By Earle R. Cressman

ABSTRACT

Chemical analyses of nondetrital siliceous sediments and sedimentary rocks—chert, siliceous earth, siliceous ooze, siliceous shale—culled from the literature have been grouped according to the following classification:

Bedded:
  Diatomaceous deposits
  Radiolarian deposits
  Sponge-spicule deposits
  Bedded chert containing few or no siliceous skeletal fragments.
Nodular

Mineralogically, the rocks consist of biogenic and chemogenic opal, chalcedony, and quartz, singly or as mixtures, admixed with the same clastic and authigenic minerals that are in the associated nonsiliceous sedimentary rocks. Opaline tests consist originally of truly amorphous silica, but much sedimentary opal has been shown by many authors to give an X-ray pattern of cristobalite or tridymite.

Small amounts of Al, Fe, and alkali and alkali-earth elements may occur within the lattice of the silica minerals; however, most of these elements are apparently in the admixed clastic and authigenic minerals, and the chemical composition of the rocks can, for the most part, be interpreted as the result of the mixture of mudstone or sandstone with pure SiO_2 or by the replacement of calcite or dolomite in carbonate rocks by pure SiO_2. Compositional differences between the rock types reflect (1) the association of diatomaceous rocks with pyroclastics, (2) the association of radiolarian rocks with argillaceous and volcanic rocks of bathyal and possibly abyssal origin, (3) the association of spicular rocks with sublittoral sandstone and limestone, and (4) the common occurrence of nodular chert in limestone of sublittoral origin.

Recent work suggests that chert cannot form by direct inorganic precipitation of silica from sea water except locally in areas of volcanism and supports the hypothesis that much bedded chert has resulted from the accumulation of siliceous skeletal remains and that most nodular chert has resulted from the replacement of carbonate rock. Many authors report abundant evidence that silica deposited as skeletal remains or in volcanic ash dissolves, migrates, and reprecipitates during diagenesis.

DEFINITIONS

Chert, by most modern American usage, is a dense cryptocrystalline rock composed dominantly of quartz, chalcedony, or opal, either singly or as mixtures, and having a tough splintery to conchoidal fracture (Tarr, 1938). As used in this report, chert is a general term that includes flint, a translucent variety with a conchoidal fracture; jasper, an opaque, red, yellow, brown, or green variety; and novaculite, a pure, dense, even-textured, light-colored variety with a porcelaneous texture. Diatomaceous, radiolarian, and spicular chert are varieties that contain conspicious skeletal remains of the type specified. Two varieties of radiolarian chert frequently described in the literature are lydite (lydian stone or culm-type), a black radiolarian chert, and radiolarian jasper.

Diatomite, radiolarite, and spiculite are rocks that consist largely of diatom frustules, radiolarian tests, or sponge spicules, but do not exhibit the characteristic physical properties of chert; as used in this report, these terms include the diatomaceous, radiolarian, and spicular earths. Their equivalents on present sea and lake bottoms are diatom, radiolarian, and spicule ooze.

Siliceous shales are rocks that consist mainly of fine-grained detrital minerals but contain noteworthy amounts of nonfragmental silica. Varieties are diatomaceous, radiolarian, and spicular shale and their equivalent muds in present sea and lake bottoms. Logically, the siliceous mudstones should not be treated in this section, but the distinction between siliceous mudstone and rocks composed dominantly of nonfragmental silica is not always made; much of the sediment called diatom or radiolarian ooze in the literature actually consists largely of detrital minerals, and the terms lydite and radiolarian jasper have been applied both to rocks composed almost entirely of nonfragmental silica and to siliceous mudstones.

Silcrete is a term applied to silicified layers in unconsolidated surficial material. The name was coined by Lamplugh (1907), who applied it to silicified surface layers in southern Africa. The term is used widely by South African geologists.

Stratigraphic nomenclature used is that of the published sources and is not necessarily that of the U.S. Geological Survey.

CLASSIFICATION AND OCCURRENCE

The analyses of the nonfragmental siliceous rocks have been organized in accordance with a classification modified from that of Hatch, Rastall, and Black (1938, p. 198) that is based on gross morphology (bedded or nodular), the relative amounts of organic and inorganic silica, and the type of siliceous organisms present. A mineralogic classification proved impractical because of the paucity of detailed petrographic descriptions ac-

companying the analyses in the literature. For the same reason, the class boundaries in the adopted classification cannot be quantitatively defined and a general class must be reserved for analyses accompanied by only the most meager rock descriptions.

The classification, together with a brief description of the occurrence and association of each type[1] is as follows.

BEDDED NONFRAGMENTAL SILICEOUS DEPOSITS

DIATOMACEOUS DEPOSITS

[Table 3]

Diatom ooze.—Diatom ooze occurs on the sea floor in a belt around Antarctica and in an arc from the Gulf of Alaska to east of Japan (Sverdrup and others, 1942, p. 976). Deposits are found in shallower water in regions of coastal upwelling; diatomaceous mud floors part of the Gulf of California (Revelle, 1950) and exists at depths of as little as 50 meters on the continental shelf off the coast of Angola and Southwest Africa (Currie, 1953, p. 499). Diatom frustules are not the dominant constituent by weight in much oceanic diatom ooze, and the sediments might more properly be termed diatomaceous mud.

Diatom ooze is also found in some fresh-water glacial lakes where its presence depends on a relatively high silica content of the inflowing streams and the absence of diluting carbonates and detritus (Conger, 1942).

Diatomite.—These fossil diatom oozes may also be divided into marine and lacustrine types. A remarkable deposit of marine diatomite is in the Monterey Formation (Miocene) of California where as much as 1,000 feet of diatomite is present in the upper part of the formation. The Monterey also contains feldspathic sandstone, rhyolitic tuff, mudstone (some of which is black), and small amounts of phosphatic mudstone and basalt (Bramlette, 1946). Diatomite is also present in rocks of Miocene age in Algeria where it totals about one-third of a sequence that is 200 meters thick (Anderson, 1933). It is interbedded with andesitic pyroclastics, marl, and clay shale; the sequence contains some gypsum lenses and is overlain by gypsum-bearing beds. Similar deposits occur in rocks of the same age in Sicily and Italy and in the Caucasus (Anderson, 1933, p. 693).

Lacustrine diatomite is found in many parts of the world, and other than in a few desiccated Pleistocene

lakes, is nearly invariably associated with volcanics (Taliaferro, 1933, p. 36).

Diatomaceous chert.—Many diatomite deposits, both marine and lacustrine, contain beds, lenses, and nodules of chert (Taliaferro, 1933, p. 23, 26; Bramlette, 1946, p. 46), but the most striking occurrence is in the Monterey Formation in which the cherty beds comprise as much as several thousand feet of strata (Bramlette, 1946). Many of the opaline chert layers in the Menelitic Shale of the lower Tertiary Flysch of the eastern Carpathians are diatomaceous (Gawel, 1950, p. 186). The noncherty beds of the Menelitic Shale consist mostly of bituminous shale and marl that is rich in fish remains and is at least in part tuffaceous (Athanasiu and others, 1927, p. 332–337; Ksiazkiewicz, 1956, p. 406). Sediments which now comprise the Monterey accumulated at depths of not more than a few hundred meters (Bramlette, 1946, p. 9, 11), and the Menelitic Shale has been interpreted as a lagoonal deposit (Athanasiu and others, 1927, p. 337), although its occurrence in a section of turbidites suggests deeper water.

RADIOLARIAN DEPOSITS

[Table 4]

Radiolarian ooze.—Radiolarian ooze occurs today in a belt crossing the north equatorial Pacific, where it has accumulated at depths of several thousand meters. Most sediments termed radiolarian ooze are actually dominantly clay (Kuenen, 1950, p. 358).

Radiolarite.—Radiolarite is present in the lower Tertiary throughout much of the Lesser Antilles, and those on Barbados have been studied in detail by Jukes-Brown and Harrison (1892), who give excellent petrographic descriptions but only partial chemical analyses. These radiolarites are associaed with foraminiferal limestone and tuffaceous argillaceous beds and are thought by Senn (1940) to be deep-sea deposits. However, Beckmann (1953) concluded from studies of benthonic foraminifera that they were deposited at depths of 1,000 to 1,500 meters, so they are probably not analogous to the radiolarian ooze of modern abyssal depths. Radiolarites have been described from beds of Eocene age in central California by Clark and Campbell (1945), who believe them to be of shallow-water origin; facies relations strongly indicate that they could not have formed in either the abyssal or lower bathyal environments.

Radiolarian chert.—The common European practice is to divide radiolarian chert into two varieties—red or green radiolarian jasper and lydite. Lydite is particularly abundant in the lower Carboniferous of Europe.

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[1] In the notes on occurrence and association, references have been made whenever possible to summary articles, the most helpful of which have been those of Davis (1918) and Kobayashi and Kimura (1944) on the occurrence of radiolarian rocks, that of Taliaferro (1933) on the occurrence of diatomaceous rocks, and the indispensable work of Cayeux (1929) on the petrography of the siliceous rocks of France. Excellent recent summaries of the petrography, occurrence, and origin of the nonfragmental siliceous sediments are found in Pettijohn (1957, p. 432–448), Dunbar and Rodgers (1957, p. 245–255), and Carozzi (1960, p. 291–343). The literature on chert and related siliceous rocks is too vast to allow citation of more than a few examples and a few references for each type.

Radiolarian chert is commonly associated with mafic flows or tuffs or both. Many of the associated flows are spilitized. Among those radiolarian cherts not closely associated with volcanic rocks are cherts of Ordovician age in eastern New York (Ruedemann and Wilson, 1936) and cherts of Triassic to Jurassic age in western Japan (Kobayashi and Kimura, 1944, p. 158). The radiolarian cherts, particularly the jaspers, are commonly intercalated in sequences of laminated shale and graywacke (Sujkowski, 1957, p. 547; Kobayashi and Kimura, 1944, p. 100), but a few are accompanied by limestone (Sujkowski, 1932; Sinclair and Berkey, 1923, p. 90) in an assemblage similar to that in the Barbados deposits. The lydites are generally associated with carbonaceous shale; particularly noteworthy is the association with highly organic alum shale in the Silurian of Saxony and Thuringia (Leutwein, 1951; Davis, 1918, p. 326). Bedded chert with sparse radiolaria in eugeosynclinal rocks of Paleozoic age in central and western Navada is estimated by R. J. Roberts (oral communication 1959) to aggregate more than 5,000 feet thick.

Bedded manganese deposits accompany many radiolarian jaspers; many such occurrences are described in the Symposium on Manganese Deposits of the 20th International Geological Congress, particularly in the volume on Asia and Oceania. The manganese may occur either as the carbonate or as oxides. Bedded deposits of manganiferous hematite and magnetite are associated with radiolarian jasper in Japan (Tababatake, 1956).

Much controversy has existed about the depth of water in which radiolarian cherts have accumulated. Some radiolarian cherts could not have been deposited at depths of more than a few hundred meters. For example, radiolarian chert of the Leonard Formation of Texas grades into conglomerate in one direction, into limestone containing a shallow-water fauna in another, and is interbedded with limestone that contains chert pebbles and wave-worn shells (King, 1930); and radiolarian chert (Carboniferous) of Gower, England, occurs in a sequence containing coal and oölitic and crinoidal limestone (Dixon and Vaughan, 1911). However, inasmuch as coarse littoral debris can be transported to deeper waters by turbidity currents, much of the evidence cited to support shallow-water origin must be re-evaluated (Pettijohn, 1957, p. 443), and the lithologic association of most radiolarian cherts, particularly those within eugeosynclinal tracts, indicates that they accumulated in the bathyal environment or deeper.

DEPOSITS OF SPONGE SPICULES

[Table 5]

Spicule ooze.—The only reported occurrences of spicule ooze are in the Antarctic Ocean, where some spicular sediments have been found at depths of 100 to 400 meters (Lisitzin, 1960), and in Lake Baikal (Votinsev, 1948).

Spiculite.—A sediment as much as 200 feet thick that consists mostly of uncemented and loosly cemented sponge spicules occurs in the Plantagenet Series of early Tertiary age in Western Australia (David, 1950, p. 539; Hinde, 1910). Similar but thinner beds have been reported from the Marble Falls Formation (Pennsylvanian) of Texas where the spiculite has resulted from the removal of calcite from a spicule-bearing limestone (Damon, 1946).

Spicular chert.—Cayeux (1929, p. 298) has described fresh-water spicular chert associated with coal in the Stephanian of France, but nearly all other spicular cherts are marine in origin.

The lithologic association is varied. Spicular chert of the Phosphoria Formation (Permian) of Montana occupies a facies position between glauconitic sandstone and black shale and is underlain by phosphorite and overlain by dolomite and calcareous shale (Cressman, 1955); spicular chert of the Lgota Beds (Lower Cretaceous) of the Carpathians is underlain by black shale and sandstone and overlain by light-colored sandstone (Ksiazkiewicz, 1956, p. 373, 374; Sujkowski, 1933a); Spicular chert of Cretaceous age in the Paris basin (*Gaizes à Spicules* and *Spongolithes* of Cayeux, 1929, p. 253) occur in a sandy, marly sequence; and spicular chert in the Lias of the Tatra Mountains is intercalated in a complex of argillaceous limestone, some of which is red (Sujkowski, 1933a). None of these cherts is closely associated with volcanic rocks. Spicular chert of the Pumpernickel Formation (Pennsylvanian?) in western Nevada is associated with argillite and thin sandy beds; ripple marks and invertebrate tracts suggest deposition at depths of 100 meters or less (R. J. Roberts, oral communication 1959).

Siliceous sponges of the class Hyalospongia generally occur at depths of greater than 1,000 meters. Sponges of the class Demospongia are found throughout a considerable depth range, but they generally thrive only in the photic zone—that is, at depth of less than 300 meters and generally less than 50 meters (de Laubenfels, 1957, p. 771, and oral communication, 1957). Chert in the Lias of the Tatras contains mostly Hyalospongia remains and is probably a bathyal deposit (Sujkowski, 1933a), but the other spicular cherts mentioned above consist mostly of spicules from Demo-

spongia and probably accumulated in sublittoral regions.

Chert in the Lgota beds occurrs within the Cretaceous Flysch (Ksiazkiewicz, 1956, p. 373) and is a eugeosynclinal deposit, but other spicular cherts were formed either on cratons in intracratonic basins, or in miogeosynclines and the bordering unstable shelf.

OTHER BEDDED CHERT

[Table 6]

Included in this group are those bedded cherts in which siliceous organic remains are either absent, very sparse, or not reported. Examples are the chert of Carboniferous age at North Flintshire, England, which is as much as 400 feet thick and is underlain by limestone and overlain by black shale and sandstone (Sargent, 1923), the Fort Payne Chert of Mississippian age in Georgia and adjacent states which overlies black shale and underlies limestone and calcareous shale (Hurst, 1953), and the Kanawha black flint in the Pennsylvanian of West Virginia which is up to 10 feet thick and occurs in carbonaceous shale that overlies the Stockton coal (Price, 1921). In both megascopic character and lithologic association, these cherts resemble others that abound in siliceous skeletal material, particularly the spicular cherts. In the Permian of British Columbia, light-gray to black chert is interbedded with carbonaceous argillite and andesitic flows; the chert closely resembles radiolarian chert of other eugeosynclinal areas, but it contains no visibile radiolaria (Cairnes, 1937, p. 11).

The Arkansas Novaculite (Devonian and Mississippian) of Arkansas and Oklahoma and its correlative in Texas, the Caballos Novaculite, are placed in this group because, although both spicular and radiolarian cherts have been reported, especially in the dark chert members (King, 1937, p. 52; Goldstein and Hendricks, 1953, p. 428–430), most descriptions emphasize the absence of siliceous organisms.[2] Ripple marks have been observed in the novaculite in both Arkansas (Miser, 1917, p. 66) and Texas (King, 1937, p. 49), indicating a sublittoral origin for at least the light-colored rocks, but shale, some of which is black, is intimately interbedded with the dark chert. The Arkansas Novaculite contains some silicified volcanic ash near the base, and the upper member in parts of Oklahoma contain manganiferous carbonate (Honess, 1923, p. 137). Deposits of manganese oxides are associated with the novaculite in Arkansas (Miser, 1917, p. 73–75).

Cherts of the iron formations of Precambrian age are included here although they are unique in their close association and intimate interlayering with sedimentary iron deposits. Most chemical analyses in the more readily accessible literature are for the banded rock (jaspilite) rather than for the chert layers only, so they are treated very cursorily in this paper. According to James (1954, p. 279), the iron-formation of the Lake Superior region was deposited in marine waters in a basin marginal to the ocean during the initial stages of eugeosynclinal subsidence. Hough (1958) has stated the case for lacustrine deposition.

NODULAR CHERT IN CARBONATE ROCK

[Table 7]

In addition to nodules, chert lenses and layers in carbonate rock are included in this group.

Much nodular chert is concentrated in the shallow-water phases of carbonate sequences where it may replace oölite (Young, 1934, p. 165; Choquette, 1955) or bioclastic carbonate rock (Hull, 1880, p. 74, 75). Chert in the Osage Group of the Mississippi Valley region is most common in a facies intermediate between sandstone and limestone (Robertson, 1952). In contrast, Lowenstam (1942a) reports the Niagaran chert of Illinois to be confined to shaly limestone and dolomite of the interbioherm facies, and chert bands and nodules occur in dense black limestone in the Bone Spring Limestone of west Texas that probably accumulated at depths of about 150 meters (Newell and others, 1953, p. 162 and 190).

An interesting association is reported by Stout and Schoenlaub (1945, p. 9) who describe nodular and lenticular chert in marine limestone overlying coal beds in Pennsylvanian cyclothems of Ohio.

Some chert nodules are formed around skeletons of siliceous sponges (Moret, 1926, p. 63; Laird, 1935, p. 257; McKee, 1938, p. 77–100), and others contain numerous sponge spicules (Lowenstam, 1942b, p. 825–828; Andrusov, 1932). Some nodules consist largely of replaced calcareous skeletal fragments (Fowler and others, 1934; Van Tuyl, 1912), or oölites (Bosazza, 1937), whereas others are uniformly aphanitic, featureless in texture.

Chert is common in both limestone and dolomite. According to Chilingar (1956), the concentration of chert nodules, stringers, and beds in limestone increases as the Ca/Mg ratio of the limestone increases.

OTHER SILICEOUS DEPOSITS

Included under this heading are siliceous sinter, silcrete, melikaria, and silicified wood. Most of these materials are more appropriately discussed in other sections, but analyses are listed in table 8 for comparison with the marine and lacustrine siliceous deposits.

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[2] Goldstein and Hendricks (1953, p. 430) believe that the paucity of siliceous organisms in the areas described by Miser (1917) and Honess (1923) is a result of dynamic metamorphism.

MINERALOGIC COMPOSITION

The opal, chalcedony, and quartz [3] in the nondetrital siliceous sediments are admixed in varying amounts with the same clastic and authigenic minerals that are present in the adjacent sedimentary rock, and with organic matter. No mineral has been reported from chert that is not also present in other sedimentary rocks, and minerals common in other marine sedimentary rocks also occur in chert.

The crystal chemistry of the silica minerals is more complex than previously thought. Summaries of recent developments and references to original work are given in two papers by Eitel (1957; 1958, p. 66–73). Especially pertinent to this discussion is evidence by Buerger (1954, p. 604–606) that small amounts of Al^{+3} replace Si^{+4} in tridymite with the excess charge compensated by alkali or alkali-earth ions in the large interstitial spaces in the tridymite structure. According to Flörke (1955a, 1955b), much low-temperature opal is not truly amorphous but contains interstratified cristobalite and tridymite layers, the tridymite layers resulting from disordering by aluminum, alkali, and alkali-earth ions. The quantity of the disordering cations may be considerable; Buerger and Lukesh (1942) report the approximate formula of tridymite from Las Plumas, Calif., as $NaCaAl_3Si_{15}O_{36}$, and Roy and Roy (1959) have synthesized cristobalite-tridymite solid solutions at high temperature that contain not less than 2 mole percent $NaAlO_2$. Quartz, on the other hand, can accommodate only Li^{+1} and possibly Be^{+2} and B^{+3} in its much smaller interstices (Buerger, 1954, p. 602). Keith and Tuttle (1952) have shown that aluminum probably substitutes for silicon in quartz with the charge compensated by lithium, and they suggest from consideration of valence requirements and ionic radii that titanium, too, can substitute for silicon, but their analyses of natural quartz (table 2) indicate that any substitution by any of these ions in quartz is very minor. In addition to these possible substitutions, Eitel (1954, p. 618) suggests that in chalcedony, the fibrous variety of quartz, ferric iron might substitute for silicon and hydroxyl for oxygen.

The silicon in siliceous organisms is in the form of opal that in diatoms, and presumably also in sponges and radiolaria, is amorphous (Mielenz and others, 1949, p. 56; Swineford and Franks, 1959, p. 117). Bramlette (1946, p. 17) states that the index of refraction in the opal of siliceous organisms varies little from 1.440 ± 0.002 which indicates a water content of about 9 percent. The water content of opal in sponge spicules ranges from 5 to 13 percent (Vinogradov, 1953, p. 184). As noted by Swineford and Franks (1959, p. 117), the opal of diatoms must be of high purity, for when diatomite is cooled from high temperature, tridymite does not form unless cations necessary to disorder the cristobalite structure have been added (Eitel, 1957, p. 146).

Mielenz, Witte, and Glanz (1949, p. 56) report cristobalite in opaline shale (but not in diatomite), and Swineford and Franks (1959, p. 117, 118) have obtained X-ray diffraction patterns of low cristobalite and tridymite from massive opal, opaline cement in sandstone, and silicified wood from the Pliocene of Kansas.

The meager data available on the relation between the mode of occurrence and the crystal structure of sedimentary opal will not permit generalizations, but they suggest that this, together with differences in composition that might be expected to accompany differences in crystal structure, would be a fruitful field for research.

A large part of both the siliceous tests and the matrix silica in deposits of Tertiary age is opaline, but nearly all of both the organic and inorganic silica in Paleozoic cherts is present as microcrystalline quartz and chalcedony.[4] Opal, quartz, and chalcedony may all be found in Mesozoic cherts. It has long been concluded from these facts that most chert was originally opaline and that opal ages to chalcedony and quartz. However, factors other than age alone are involved: Cayeux (1929, p. 694) found no difference in the mineralogic character of the silica between cherts of Mesozoic and Tertiary age in the Paris basin, and Bramlette (1946, p. 54) cites evidence that both load and deformation further the conversion of opal to quartz and chalcedony. The structure and composition of the opal might have an effect on the ease of transformation; thus opal with a tridymite structure might be difficult to convert to quartz because of the large cations in the interstices of the lattice (Eitel, 1954, p. 617). Three analyses of nearly pure cherts are listed in table 1 as standards against which less pure cherts may be compared. Trace-element analyses of several speciments of igneous and hydrothermal quartz are listed in table 2 for comparison with chert analyses.

CHEMICAL COMPOSITION

The chemical analyses in tables 3, 4, 5, 6, 7, and 8 have been selected from the more complete analyses available so as to represent a wide geographic and strat-

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[3] The fibrous-quartz varieties quartzine and lutecine and the cristobalite varieties lussatite and lussatine described in some European literature (Braitsch, 1957) are not generally distinguished by American petrographers.

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[4] For discussions of differences between microcrystalline quartz and chalcedony see Folk and Weaver (1950), Midgley (1951), and Pelto (1956). The recent tendency has been to discount the presence of any opal in the older cherts, but Hoss (1959) has advanced evidence for small amounts of opal in lower Carboniferous lydite of Germany.

igraphic range, but all appropriate analyses culled from the literature have been plotted in the diagrams.

TABLE 1.—*Analyses of three nearly pure cherts*

[Samples not analyzed for elements other than those given]

	1	2	3
SiO_2	99.82	99.95	99.86
Al_2O_3	.11	.00	.00
Fe_2O_3	.00	.00	.00
FeO	.07	.06	.06
MgO	.00	.00	.00
CaO	.00	.00	.03
Na_2O	.00	.00	.01
K_2O	.03	.01	.01
H_2O+	.03	.01	.07
H_2O-	.00	.00	.00
CO_2	.00	.00	.00
Total	100.06	100.03	100.04

Trace elements

[Parts per million]

	1	2	3
As	1.0	0.7	0.4
Ge	.2	3.0	.4
Li	2	0	0
Mn	6	3	7
Mo	2.6	1.6	1.8
P	37	15	22
Ti	82	0	23

1. White novaculite from Arkansas Novaculite (Maxwell, 1953).
2. Chalcedony nodule from clay pit, Virginia (Maxwell, 1953).
3. Siliceous cement from chert breccia, Labrador (Maxwell, 1953).

TABLE 2.—*Spectrochemical analyses of igneous and hydrothermal quartz*

[Analyses in parts per million. Modified from Keith and Tuttle, 1952, p. 224. Symbol: n.d., not determined]

	1	2	3	4
B			≈ 10	≈ 20
Cu	10-100	≈ 1	≈ 1	<1
K	n.d.	n.d.	n.d.	5-50
Li	n.d.	10-50	10-50	100-1,000
Mg	10-100	<10?	<10?	<10?
Na	1-5	1-5	1-5	10-300
Ti	10-100	n.d.	n.d.	n.d.

NOTE.—Al is present in all samples (10-100 ppm), but sample 4 is estimated to have about four times as much as sample 2. Ba and Fe are reported in small amounts in all four samples.

Ag, V, and Sr are doubtful trace elements; Mn, Cr, Ca, Ni, Pt group, In, Ga, Zr, La, Nd, Y, Be, Rb, and Cs were looked for but not found. Ge and Au were not detected in 3 and 4 and not looked for in 1 and 2.

1. Quartz crystal, Brazil.
2. Pegmatitic quartz, South Dakota.
3. Drusy incrustation on barite or celestite, Colorado.
4. Pale-green quartz, Iceland.

MAJOR CONSTITUENTS

The frequency distributions of four types of chert within the major compositional triangle SiO_2-$(Al,Fe)_2O_3$-$(Ca,Mg)CO_3$ are plotted on figure 1. The major differences between types may be explained largely by differences in lithologic association. Radiolarian rocks

TABLE 3.—*Analyses of diatomaceous rocks*

	Diatom ooze			Diatomite										Diatomaceous chert
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	60.14	61.80	82.36	71.80	89.70	79.55	71.99	71.20	79.7	86.25	83.21	73.16	78.5	87.20
Al_2O_3	13.01	9.25	4.87	5.02	3.72	8.18	3.00	12.67	6.4	.62	2.96	9.08	5.7	1.86
Fe_2O_3	5.96	3.43	2.23	2.45	1.09	2.62	1.12	5.65	1.1	.80	.33	1.44	1.9	1.06
FeO				.35				.38						.33
MgO	2.34	2.82	1.84	1.69	.65	1.30	2.30	.40	Tr.	.31	Tr.	.23	.8	1.14
CaO	1.87	4.19	7.85	1.45	.35	.25	8.15	1.35	.5	.45	.20	.50	1.4	.05
Na_2O	1.97	3.10	Tr.	1.81	.82	1.31	.63		.08		.20	1.20	.8	.53
K_2O	2.04	1.45	Tr.	3.55				.46	.06		.17	1.40	1.1	2.75
H_2O+	8.01			5.50				7.91	5.0	5.74	8.81	7.20		2.23
H_2O-				4.64										2.78
Loss on ignition					3.70	5.80	12.68		7.4	5.48	4.00	5.41		
TiO_2	.53	.42			.10	.70	.13		.3		.09	.21	.25	
P_2O_5	.12		.09	.17										.22
MnO	.74	.17	.10						.01					
Total	[1] 98.13	[2] 86.66	[3] 99.35	[4] 99.77	100.13	99.71	100.00	[5] 100.27	100.55	99.65	99.97	99.83		[6] 100.31

[1] Includes CO_2, 0.20; C, 1.20.
[2] Includes SrO, 0.033.
[3] Includes ZrO_2, 0.01.
[4] Includes Cl, 1.34; a small amount of C present.
[5] Includes SO_3, 0.25.
[6] Includes Cl, 0.16; a small amount of C present.

1. Diatom ooze, North Pacific (Revelle, 1944, p. 59). Sharp-Schurtz Co., analysts.
2. Diatomaceous sediment with volcanic ash layers (Goldberg and Arrhenius, 1958, p. 170).
3. Average of six Arctic diatom oozes (Sujkowski, 1952).
4. Composite sample of 10 diatomaceous rocks, Monterey Formation (Miocene), California (Bramlette, 1946, p. 13). R. C. Wells, analyst.

5. Diatomite, Monterey Formation, California (Cummins and Mulryan. 1949).
6. Diatomite (marine), Tertiary, Maryland (Cummins and Mulryan, 1949).
7. Diatomite (marine), Miocene, Algeria (Cummins and Mulryan, 1949).
8. Diatomite, Tertiary, Siberia (Maleev, 1937).
9. Diatomite (lacustrine), Tertiary, Queensland, Australia (Bonner, 1951).
10. Diatomite (lacustrine), Miocene. Washington (Glover, 1936).
11. Diatomite (lacustrine), Pleistocene, New Zealand (Grange, 1937). F. T. Seelye, analyst.
12. Diatomite (lacustrine), Pleistocene, New Zealand (Grange, 1937). F. T. Seelye, analyst.
13. Average of analyses 4 through 12.
14. Composite sample of 10 chert shales, Monterey Formation (Miocene), California (Bramlette, 1946, p. 13). R. C. Wells, analyst.
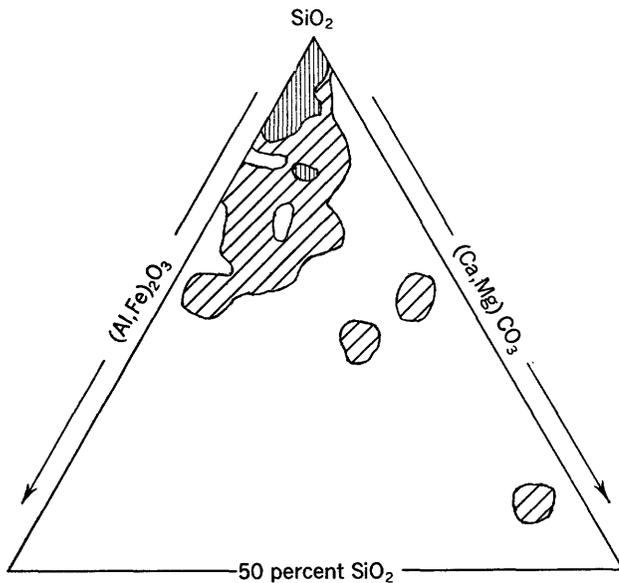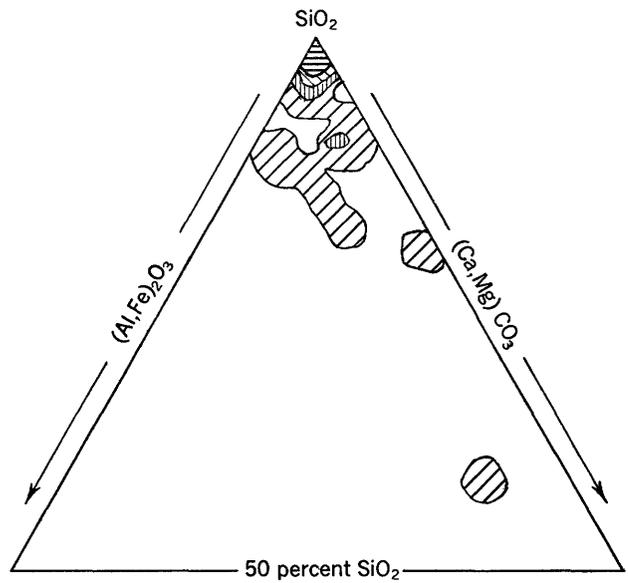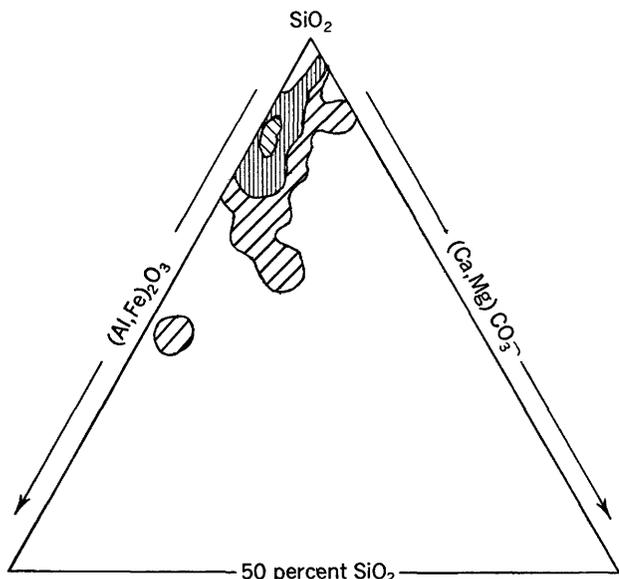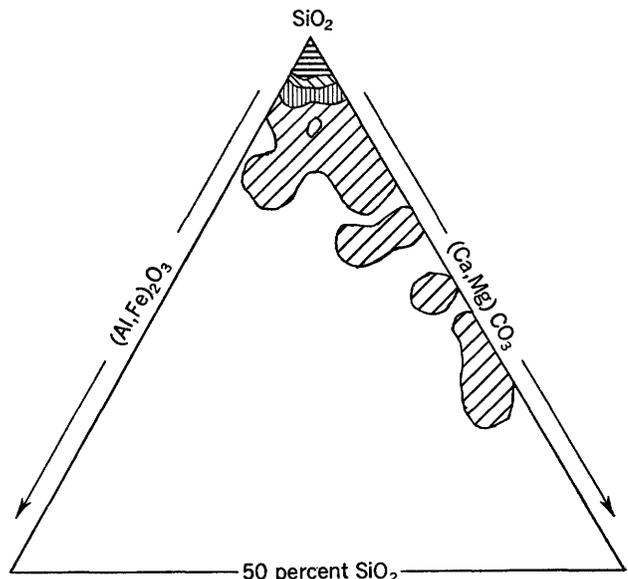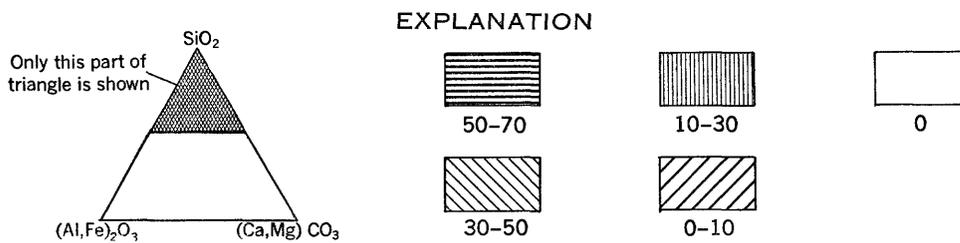
FIGURE 1.—Frequency diagrams of four types of nonfragmental siliceous sedimentary rocks. Analyses were plotted in the SiO_2-$(Al,Fe)_2O_3$-$(Ca,Mg)CO_3$ compositional triangle, tallied by use of a 1-percent-area triangle, and contoured. Only that part of the triangle containing more than 50 percent SiO_2 is shown.

TABLE 4.—Analyses of radiolarian rocks

	Radiolarian ooze		Black radiolarian chert						Red and green radiolarian chert (radiolarian jasper)					Av. (3–13)
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	66.67	64.34	95.94	97.6	91.06	86.9	89.6	89.15	76.54	83.67	94.90	88.20	95.00	89.9
Al_2O_3	14.82	15.37	1.39	.8	3.79	4.6	4.8	3.45	10.65	3.30	2.31	4.40	1.70	3.7
Fe_2O_3	6.51	6.85	.69	.15	2.01	2.7	1.6	.58	4.02	7.74	1.19	3.91	.78	2.3
FeO			.05					2.19					.11	
MgO	2.58	3.58	.26	Tr.	.46	.8	.4	1.05	.79	.50	.30	1.25	.23	.5
CaO	2.26	1.86	.00	Tr.	.45	.1	.2	.24	.48	.40	.30	.30	.41	.3
Na_2O	1.66	.98	.13	.02	.28	.4	.3	.22	4.40	1.00	.50	.60	.09	.7
K_2O	2.54	3.75	.53	.1	.84	1.0	.8	.53	1.03	1.42			.33	.7
H_2O+				.60	.97	2.3	2.3	1.17	.70	.85	1.35	1.25	.71	
H_2O-			.06	.08	.32	.3	.1		.00	.10			.08	
Loss on ignition			.42											
TiO_2	.63	.73	Tr.	.02		.14	.10	.22	.57	.40	.10	.20	.08	.2
P_2O_5	.14	.46	.02	.44	Tr.	.04	.04	.04	.13	.10	Tr.	Tr.	.20	.9
MnO	.28	.29	.01	.04	Tr.	.03	.10	.03	.61	.30			.18	.1
CO_2	.51	.70	.00						.00				.06	
C	1.32	.89	.30		Tr.	.65	.13	.11						
Total	[1] 99.94	[2] 99.93	[3] 99.80	99.85	100.18	99.96	100.47	[4] 99.71	[5] 99.92	99.78	100.95	100.11	[6] 99.97	

[1] Includes ZrO_2, 0.02.
[2] Includes ZrO_2, 0.13.
[3] Also FeS_2, trace.
[4] Includes ZrO_2, 0.59; S, 0.14.
[5] BaO, 0.00.
[6] Includes Li_2O, 0.01.

1–2. Radiolarian ooze from North Pacific (Revelle, 1944, p. 58, 59). Recalculated to sea-salt-water and water-free basis. Sharp-Schurtz Co., analysts.
3. Black radiolarian chert, Upper Silurian, Carnic Alps, Austria (Heritsch and Heritsch, 1943).
4. Black radiolarian chert, Silurian, Altmannsgrun, Saxony, Germany (Hoss, 1957, p. 81).
5. Black radiolarian chert, Devonian, New South Wales, Australia (David and Pittman, 1899). J. C. H. Mingaye, analyst.
6. Black radiolarian chert, lower Carboniferous (Culm), Wallace, Hesse, Germany (Hoss, 1957, p. 65).

7. Black radiolarian chert, Harz Mountains, Germany (Hoss, 1957, p. 81).
8. Red and green radiolarian chert, Pumpernickel Formation (Lower Permian), Antler Peak quadrangle, Nevada (R. J. Roberts, U.S. Geological Survey, unpublished data). M. K. Carron, analyst.
9. Bright red radiolarian chert, Jurassic, Val d'Err, Switzerland (Jakob, 1925).
10. Red radiolarian chert, Jurassic, Val d'Err, Switzerland (Jakob, 1925).
11. Red radiolarian jasper, Jurassic(?), Borneo (Cayeux, 1929). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
12. Red radiolarian jasper, Eocene, Tuscany, Italy (Cayeux, 1929). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
13. Radiolarian chert, Franciscan Formation, Jurassic near Oakland, Calif. (Maxwell, 1953).
14. Average of analyses 3 through 13.

TABLE 5.—Analyses of spicular chert

	1	2	3	4	5	6	7	8	9
SiO_2	94.10	94.6	82.94	98.60	94.75	94.63	85.70	64.00	88.7
Al_2O_3	1.85	1.8	.1	.39	1.30	2.23	3.88	5.23	2.1
Fe_2O_3	1.65	.36	3.4	.21	.55	1.74	2.07	2.47	1.5
FeO			.28						
MgO	.01	.64	.19			.18	.49	.81	.4
CaO	.05	.49	1.60	.26	Tr.	.91	1.05	11.67	2.0
Na_2O		.15	.65	.11	.37	18	.20	.36	.3
K_2O		.37	1.40		.21		.68	.08	.5
H_2O+	2.45	.77	.33		2.35		5.80	6.45	
H_2O-		.09							
TiO_2		.07	.27	.11		.10	.30	.30	.2
P_2O_5		.24	.8				Tr.	.10	
CO_2		.60	.40					7.90	
Total	100.11	[1] 100.49	[2] 92.38	99.68	99.53	99.97	100.17	99.37	

[1] Includes MnO, 0.03.
[2] Includes F, 0.10; S, 0.14; V_2O_5, 0.06.

1. Lacustrine?, Stephanian, France (Cayeux, 1929, p. 299). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
2. Pumpernickel Formation (Lower Permian), Antler Peak quadrangle, Nevada (R. J. Roberts, U.S. Geological Survey, unpublished data). K. White, H. F. Phillips, P. W. Scott, and F. S. Borris, analysts.
3. Phosphoria Formation (Permian), Utah (Smith and others, 1952, p. 12). Analysis by Tennessee Valley Authority.
4. Jurassic, Poland (Morawiecki, 1955).
5. "Spongolithe", Cretaceous, France (Cayeux, 1929, p. 416). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
6. Lgota Beds, Cretaceous, Poland (Kamienski and Tokarski, 1958).
7. "Gaize", Cretaceous, France (Cayeux, 1929, p. 259). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
8. "Gaize", Cretaceous, Belgium (Cayeux, 1929, p. 212). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
9. Average of analyses 1 through 8.

are most abundant in argillaceous sequences and both radiolarian and diatomaceous rocks are very commonly associated with pyroclastics; they are therefore somewhat more aluminous that the spicular cherts which are more commonly associated with sandstone or carbonate rocks. The similarity between spicular and nodular cherts reflects their common origin in relatively shallow water in which clay is not so likely to accumulate.

The relations between SiO_2 and Al_2O_3 are further illustrated by figure 2 on which SiO_2 is plotted against the ratio SiO_2/Al_2O_3. The radiolarian rocks fall along a well-defined trend that is marked by curve A, the theoretical change in composition that would result from the addition of SiO_2 to a siliceous ooze of the composition of the average of the six reported by Revelle (1944, p. 58). The line would fit the trend of the radiolarian rocks equally well if plotted from either the average pelagic clay or the average shale. The trend reflects the occurrence of radiolarian chert in carbonate-poor very argillaceous rocks.

The spicular rocks form a somewhat less well-defined trend, most of the samples having a higher SiO_2/Al_2O_3 ratio than radiolarian rocks with the same SiO_2 content, as one might expect from the common association of spicular chert with sandstone. Curve B, similar to curve A, but plotted from the composition of the average sandstone (Clarke, 1924, p. 30), fits the trend fairly well.

Part of the wide spread of the diatomaceous rocks on figure 2 results from the high content of organic matter of some, particularly those from high-latitude lacustrine deposits, and the high-water content of others.

No regular relationship is apparent between SiO_2 and the ratio SiO_2/Al_2O_3 for nodular chert on figure 2. Curve C is the change in composition that would result from the addition of SiO_2 to the average limestone, the composition of which is taken from Clarke (1924, p. 30).
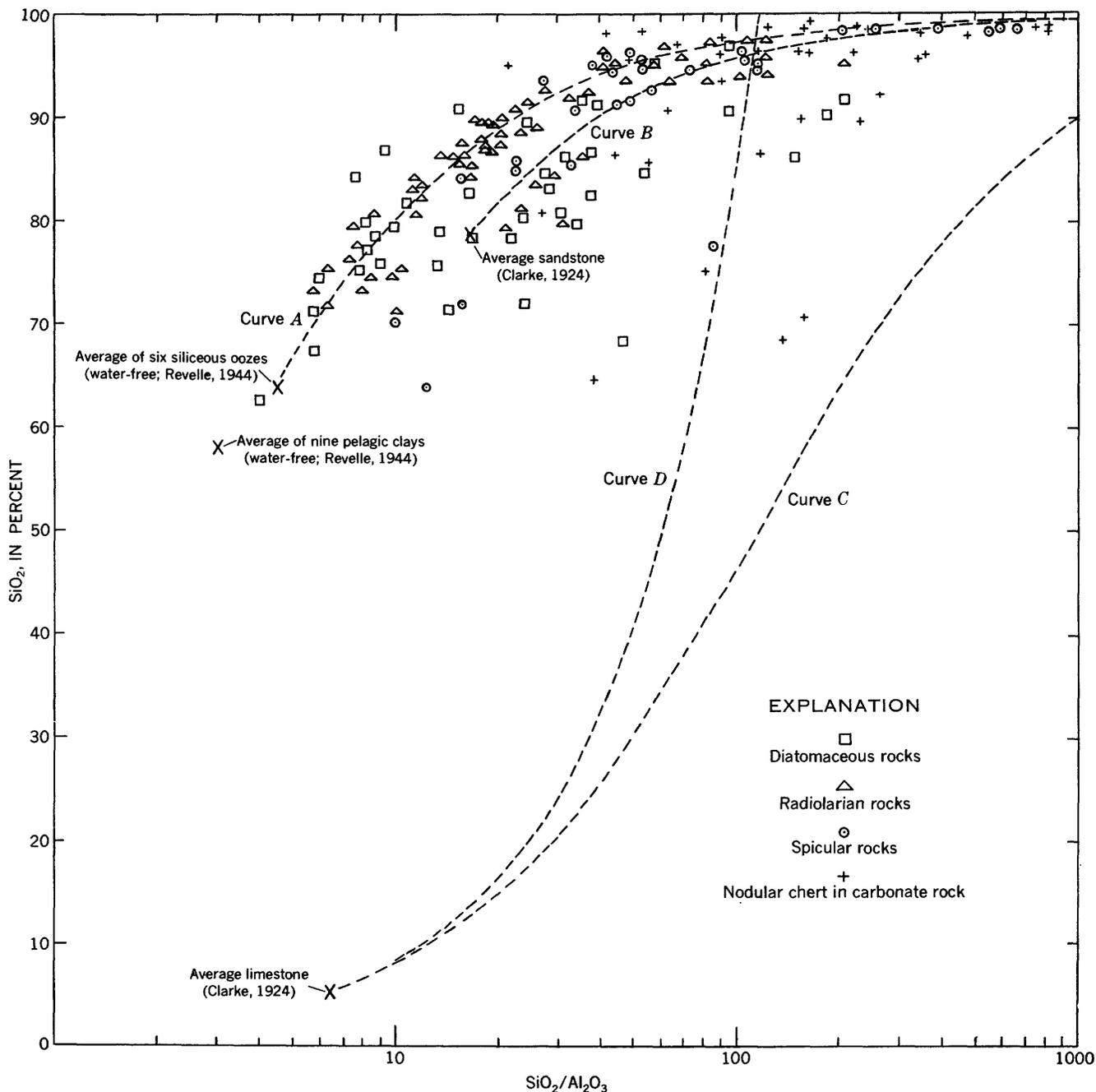
FIGURE 2.—Relation between SiO₂ and the ratio SiO₂/Al₂O₃ in chert and related rocks.

It is not surprising that many analyses lie above curve C inasmuch as many nodular cherts exhibit replacement textures, but it is surprising that all lie above the curve. Clark's average limestone may be too low in SiO_2 and Al_2O_3, or nodular chert may develop preferentially in rock more sandy or argillaceous than the average limestone, but most of the points remain above the curve if it is constructed from any reasonable initial composition. Curve D is the change of composition that would

result from volume-for-volume replacement of calcite of the average limestone by quartz. The curve at least falls in the midst of the points, but there is no similarity between the arrangement of the points and the trend of the line. The absence of any trend in these analyses may be explained partly by a wide range in the composition of the parent rock. Furthermore, even cherts with evident replacement textures probably have resulted from both replacement and pore filling so that

TABLE 6.—*Analyses of bedded cherts containing few or no siliceous skeletal remains*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	99.43	61.42	96.39	95.89	99.47	99.66	97.80	99.33	74.56	93.75	92.86	80.59	97.74	85.40
Al_2O_3	.01	.10	.78	1.95	.23	.03	.60	.01	3.23	2.63	1.95	8.29	.44	2.06
Fe_2O_3	.03	30.64	.43	.24	.00	.00	.06	.08	5.23	1.43	2.28	1.83	.09	1.43
FeO	.16	3.23		.13	.09	.15	.23	.23	.00	.00			.70	.14
MgO	.01	.20	.05	.05	.00	.00	.03	.01	3.60	Tr.	.10	.34	.25	.12
CaO	.08	.48	.23	.04	.00	.00	.18	.00	6.26	1.36	.27	.70	.33	4.56
Na_2O	Nil	.94	.04	.04	.01	.01	.03	.01			.77	1.82		.25
K_2O	Nil			.30	.05	.01	.15	.03	Tr.	.00				.35
H_2O+	.16	.08	.96	1.03	.07	.11	.50	.17	.05	.00	.23	.53	.53	1.80
H_2O-	.01	1.79	.16	.15	.01	.02	.14	.05					.07	.10
Loss on ignition											2.03	6.55		
TiO_2			.051	.091				.034	Tr.	.00			Nil	.15
P_2O_5			.071	.047			.105		.00	.00				1.62
MnO									.01	.02				.01
CO_2	.06	.66	.01	.00	.01	.00	.00	.00	5.85	1.00			Nil	2.06
C	Nil		.31	.15										
SO_3									1.30	.00				
Total	99.95	99.54	99.48	100.11	99.94	99.99	99.83	99.95	100.09	100.19	100.49	100.65	100.15	100.05

1. Chert band, Soudan Iron-Formation, Precambrian, Minnesota (Maxwell, 1953).
2. Chert band from iron-formation, Precambrian, India (Spencer and Percival, 1952)
3. Bedded chert, Maravillas Formation, Ordovician, Texas (Maxwell, 1953).
4. Huntersville Chert of Price (1928), Devonian, West Virginia (Maxwell, 1953).
5. Gray Arkansas Novaculite, Devonian, Arkansas (Maxwell, 1953).
6. Milky-white novaculite, lower novaculite member of Caballos Formation, Devonian, Texas (Maxwell, 1953).
7. Banded chert, upper chert member of Caballos Formation, Devonian, Texas (Maxwell, 1953).
8. White to light-buff novaculite, upper novaculite member of Caballos Formation, Devonian, Texas (Maxwell, 1953).

9-10. Fort Payne Chert, Mississippian, Georgia (Hurst, 1953). L. H. Turner, analyst.
11. Kanawha flint, blocky phase, Pennsylvanian, West Virginia (Price, 1921). J. B. Krak, analyst.
12. Kanawha flint, shaly phase, Pennsylvanian, West Virginia (Price, 1921). J. B. Krak, analyst.
13. Light to dark-gray chert interbedded with greenstone and argillite, Fergusson Series, Permian(?). British Columbia (Cairnes, 1937). R. J. C. Fabry, analyst.
14. Chert interbedded with limestone, siltstone, and phosphorite, Jurassic, Zacatecas Mexico (Rogers and others, 1956, p. 19). Alberto Obregón, analyst.

TABLE 7.—*Analyses of chert nodules, lenses, and layers in carbonate rock*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	98.30	95.00	99.47	98.63	95.11	95.72	70.78	64.55	96.45	86.11	98.36	92.30	97.54	91.4
Al_2O_3	1.85	4.47	.06	.12	.14	.32	.45	1.67	.07	1.92	.12	.35	.52	.9
Fe_2O_3	.04	.61	.00	.00	.40	.09	.02	1.03	.07	.88	.00	.60	.19	.3
FeO			.17	.09	.44	.12	.30		.06		.08			.2
MgO	.07	.07			.71	.21	1.88	5.45	.49	.20	.01	.10	Nil	.8
CaO	.02	.01	.06	.45	1.11	1.25	12.90	10.80	1.25	5.40	.16	2.25	Nil	2.7
Na_2O			.01	.01	<.01	.04	.05	.53	.01	.42	.04	.29		.1
K_2O			.03	.02	.01	.10	.06		.04		.04			.05
H_2O+			.19	.13	.25	.55	.48	1.70	.35	.80	.84	2.05	.28	
H_2O-			.02	.08	.43	.11	.32		.03		.11			
Loss on ignition	.22	.32											1.12	
TiO_2	Nil	Nil			.03	.027	.03		.018			Tr.		.02
P_2O_5					.01	.009	.16	Tr.	.033		.023	Tr.		.03
MnO	Nil	Tr.			.01	.002	.02							
CO_2			.00	.25	1.38	1.17	12.04	13.90	1.20	4.10	.07	1.45		3.6
C			.03	.03	.05	.04	.33				.02			
Total	100.50	100.48	100.04	99.81	[1] 100.29	99.76	[2] 100.09	99.63	100.07	99.83	99.87	99.39	99.65	

[1] Includes FeS_2 0.21, SO_3 <0.01.
[2] Includes ZrO_2<0.01, FeS_2 0.27, SO_3 <0.01.

1-2. Chert bands, dolomite series, Precambrian, South Africa (Bosazza, 1937).
3. Oölitic chert, mines Dolomite, Cambrian, Pennsylvania (Maxwell, 1953).
4. Chert, Ellensberger Group, Ordovician, Texas (Maxwell, 1953).
5. Chert layer in dolomite, Bisher Formation, of Foerste (1917), Silurian, Ohio (Stout and Schoenlaub, 1945). Downs Schaaf, analyst.
6. Chert, Keyser Limestone, Devonian, West Virginia (Maxwell, 1953).
7. Chert nodule, Delaware Limestone, Devonian, Ohio (Stout and Schoenlaub, 1945). Downs Schaaf, analyst.
8. Chert from dolimite, Carboniferous, France (Cayeux, 1929, p. 533). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.

9. Chert, Bird Spring Formation, Pennsylvanian, Nevada (Maxwell, 1953).
10. Chert nodule, Jurassic, France (Cayeux, 1929, p. 495). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
11. Flint nodule, Dover Chalk, Cretaceous, England (Maxwell, 1953).
12. Flint nodules, Cretaceous, France (Cayeux, 1929, p. 437). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
13. Chert, Amuri Limestone, Cretaceous(?), New Zealand (Wellman, 1945). L. R. L. Dunn, analyst.
14. Average of analyses 1 through 13.

two parent rocks with the same initial composition but different porosities would, on silicification, yield cherts of different composition.

The assumption has been made in this discussion that most of the aluminum occurs in terrigenous clays with some contribution from feldspars and other aluminum silicates. This is generally confirmed by petrographic studies (for example, see Bramlette, 1946, p. 17–18, and Hoss, 1957). However, Robertson and Twedily (1953) report that late Pleistocene or Recent diatomite from Skye contains 5 to 60 percent of an alumina-ferric oxide-silica gel, which might partly explain the scatter of the diatomaceous rocks on figure 2, and aluminum may substitute for silicon in the cristobalite-tridymite lattice of opaline chert. Vinogradov (1953, p. 103, 180, 181) lists analyses of siliceous sponges in which the combined Al_2O_3–Fe_2O_3 is as much as 10 percent of the total ash, but inasmuch as sponges are filter feeders, much of the alumina may be in foreign clay particles.

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Nodular chert generally contains less than 1 percent total iron as Fe_2O_3; most bedded chert contains more than 1 percent Fe_2O_3, and the content of some red radiolarian cherts ranges up to nearly 9 percent (Jakob,

TABLE 8.—*Analyses of silcrete and other siliceous materials*

	1	2	3	4	5	6	7	8
SiO₂	95.35	94.72	99.95	85.2	96.84	83.50	85.58	92.6
Al₂O₃	.36	.55	.00	1.1	.02	.78	.74	1.0
Fe₂O₃	1.81	1.74	.00	.26	.00	.32	.09	.23
FeO			.06	.20	.05			.14
MgO	.09	.23	.00	.48	.11	1.82	.01	.07
CaO	.33	.63	.00	5.7	1.54	3.85	.64	.36
Na₂O	Nil		.00	.18	.01	.21	.58	.41
K₂O	.02		.01	.16	.01	.27	.28	.21
H₂O+			.01	1.0	.26	} 6.40	{ 5.50	
H₂O−			.00		.03		6.17	5.5
Loss on ignition	.73	.34					.03	.04
TiO₂	1.26	2.13		.04			.01	.02
P₂O₅				.24			.02	.42
MnO				.02				
CO₂			.00	4.8	.64	2.60	.00	
Total	99.95	100.34	100.03	99.4	[1]99.57	99.75	[2]99.77	101.0

[1] Includes C 0.06.
[2] Includes S 0.09, BaO 0.03.

1. Silcrete, Australia (Williamson, 1957). B. C. Terrell, analyst.
2. Silcrete overlying lower Dwyka Shale, South Africa (Frankel and Kent, 1937). J. J. Frankel, analyst.
3. Chalcedony nodule in clay, Virginia (Maxwell, 1953).
4. Silicified oölite from beneath tuff bed, Twin Creek Limestone, Jurassic, Lincoln County, Wyoming (E. R. Cressman, U. S. Geological Survey, unpublished data). S. D. Botts, M. D. Mack, and H. H. Thomas, analysts.
5. Petrified wood, Arizona (Maxwell, 1953).
6. Chert nodule from gypsum, Eocene, France (Cayeux, 1929, p. 672). Laboratorie de Chimie de la Préfecture de Police, M. Lassieur, director.
7. Siliceous sinter, New Zealand (Grange, 1937, p. 118). F. T. Seelye, analyst.
8. Primary opaline sinter, Steamboat Springs, Nevada (D. E. White, U.S. Geological Survey, unpublished data). H. F. Phillips, Leonard Shapiro, and Katrine White, analysts.

1925).[5] Much of the iron in the red radiolarian jaspers is in the form of hematite (Cayeux, 1929, p. 324), in unweathered black radiolarian chert as pyrite (Hoss, 1957, p. 62; Cayeux, 1929, p. 333), and in spicular chert as glauconite or pyrite or both (Cayeux, 1929, p. 255–301). In those cherts containing admixed pyroclastic material, iron may occur in augite, hornblende, magnetite, and ilmenite, and the work of Robertson and Twedily (1953) suggests that much iron in the younger diatomaceous rocks may be in an alumina-ferric oxide-silica gel.

The iron content of bedded chert is generally less than that of the associated sediments. For example, the average Fe₂O₃ content of 13 samples of black radiolarian chert from the Carboniferous of Germany is 2.4 percent, whereas six interbeds of argillite average 3.6 percent (Hoss, 1957, p. 65, 67). Even the high-iron content of the red radiolarian chert analyzed by Jakob is less than that found in many red clays (Clarke, 1924, p. 516; Ishibashi and Harada, 1938).

On figure 3, the total iron as Fe₂O₃ is plotted against Al₂O₃ for analyses of radiolarian chert. The Fe₂O₃/Al₂O₃ ratio in most of the radiolarian cherts is about

[5] Chert from iron formations of Precambrian age may, of course, contain much more iron.
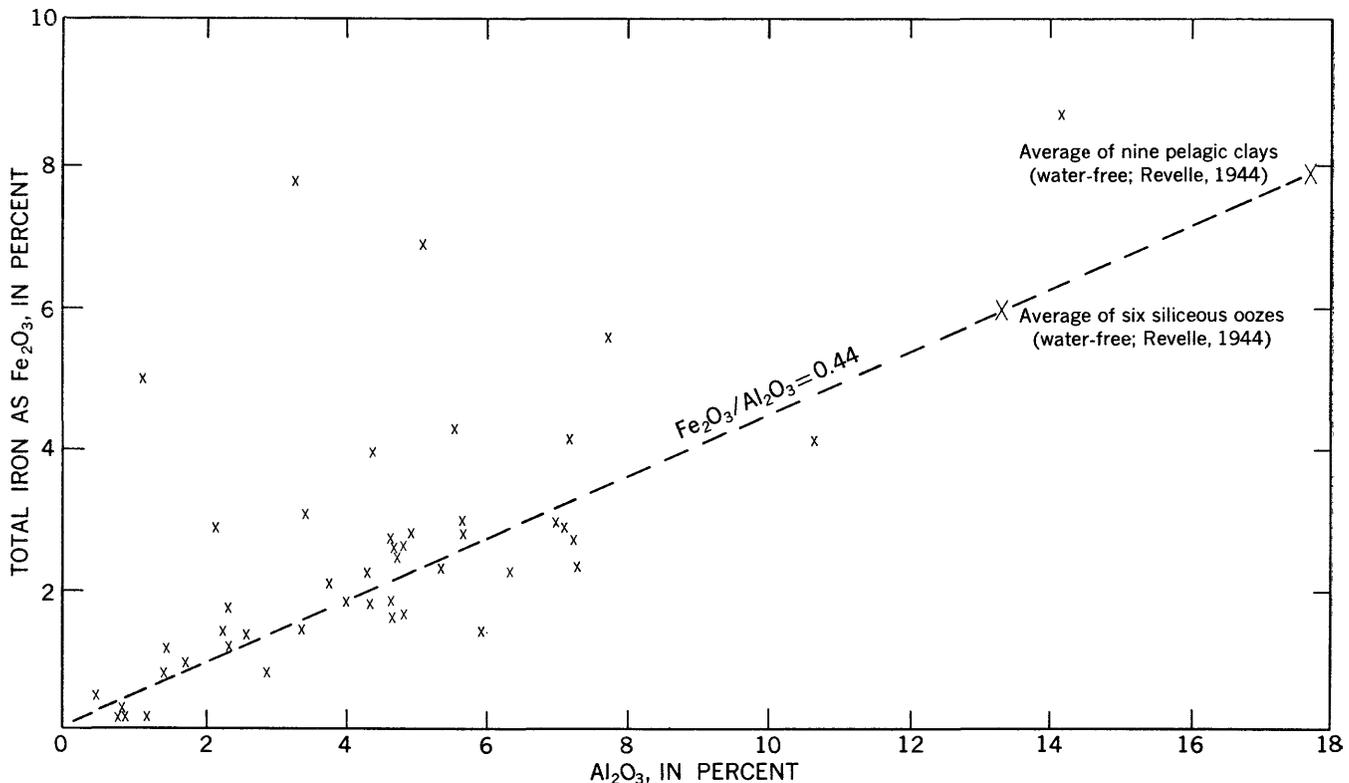

FIGURE 3.—Relation of Fe₂O₃ to Al₂O₃ in 46 radiolarian cherts.

the same as in modern pelagic clay and siliceous ooze, and the iron content may be explained by the addition of SiO_2, either as radiolarian tests or as inorganic silica, to typical marine lutite. However, a few radiolarian jaspers contain considerably more iron than can be explained in this manner. Inasmuch as these high-iron cherts are associated with volcanic rocks, the iron may have had a local source.

Excluding the sample from the Phosphoria Formation, the Fe_2O_3/Al_2O_3 ratios of the spicular chert listed in table 3 are all less than 1 and average 0.53, only slightly more than 0.44, the ratio in the average shale (Clarke, 1924, p. 30). Spicular chert of the Phosphoria Formation at one locality in Montana contains 2.8 to 4.9 percent Fe_2O_3, about the same as in interbedded mudstone, but the Fe_2O_3/Al_2O_3 ratio in the chert averages 3.1 as compared with 0.61 in the mudstone (Swanson and others, 1953, p. 29). The iron in chert of the Phosphoria Formation is now present as pyrite, but inasmuch as these cherts occur in the upper part of a highly carbonaceous black shale sequence, the immediate source of much of the iron may have been organic matter, for marine plants are known to concentrate iron (Harvey, 1955, p. 144).

Too few analyses are available to compare the iron content of chert nodules with that of the country rock, but a few such analyses (Bosazza, 1937, p. 182; Cayeux, 1929, p. 495, 498; Lamar, 1953, p. 26) suggest that the content does not differ markedly. However, Newell and coworkers (1953, p. 162) note that chert lenses and nodules in the Bone Spring Limestone (Permian) of Texas commonly contain more pyrite than the surrounding limestone.

MANGANESE

The manganese content of chert is of particular interest because of the association of sedimentary manganese deposits with radiolarian chert. A number of radiolarian cherts, both lydites and jaspers, contain 10 or 20 times as much manganese as the average igneous rock or the average shale (fig. 4 and table 4), but none of the cherts for which analyses are available is more enriched than much of the siliceous ooze and clay of the oceanic basins. However, Taliaferro and Hudson (1943, p. 237) describe manganiferous opal in chert of the Franciscan formation that must contain considerably more manganese than any samples on figure 4 or table 4.

The analyses of the Arkansas and Caballos Novaculites are all much lower in manganese than are those of other bedded cherts, the highest value reported being 0.0011 percent Mn. However, the upper part of the Arkansas Novaculite in parts of Oklahoma and Arkansas contains as much as 0.41 percent Mn in the form

of either manganiferous calcite or rhodochrosite (Miser, 1917, p. 80; Goldstein and Hendricks, 1953, p. 430; Crittenden, in Hewett and others, 1956, p. 188).

The manganese content of chert in carbonate rock is generally quite low, nearly all samples containing less than 0.01 percent Mn. Pieruccini (1951a, p. 52) lists the manganese contents of 17 chert layers and nodules from Mesozoic limestone of the central Apennines; the average content is 0.0052 percent Mn (0.0067 percent MnO) and the highest value 0.020 percent Mn (0.026 percent MnO). Pieruccini's samples are therefore somewhat more manganiferous than the nodular cherts plotted on figure 4, but they are considerably less manganiferous than most bedded cherts. The few available analyses show that chert nodules contain considerably less manganese than the surrounding carbonate rock (Pieruccini, 1951a, p. 52; Bosazza, 1937, p. 182), as might be expected if most of the manganese were originally present in the calcite of the parent rock.

RELATION OF IRON TO MANGANESE

The iron and manganese contents of chert and related siliceous sediments are plotted on figure 4. In general, the iron content increases but the ration of Fe/Mn decreases as the manganese content increases. The Fe/Mn ratio is higher in nonvaculite and nodular chert, both of which are associated with sublittoral sediments, than it is in radiolarian chert. Correns (1937) reports a higher Fe/Mn ratio in shallow-water sediments than in deep-water sediments in the equatorial Atlantic. Comparison of the ratios in radiolarian rocks (the average Fe/Mn ratio of all radiolarian cherts in table 4 is 20) with those in the following table, recalculated from Correns' data, supports the interpretation of most radiolarian cherts as bathyal or abyssal deposits:

TABLE 9.—*Relation of iron and manganese to depth of water in sediments of the equatorial Atlantic Ocean*

[Recalculated from Correns, 1937, p. 231]

	Values for iron and manganese for indicated depth range in meters					
	0–200	200–2,000	2,000–3,000	3,000–4,000	4,000–5,000	5,000–6,000
Fe	2.60	4.27	4.98	5.64	4.77	4.79
Mn	.0294	.0573	.394	.320	.238	.525
Fe/Mn	88.0	75.0	12.6	17.6	20.0	9.0

The explanation of the concentration of manganese relative to iron in deep-sea sediments that was originally advanced by Murray and Irvine (1895) and was recently supported by Krauskopf (1957, p. 78) is that manganese oxide precipitated in shallow-water sediments is reduced in the presence of organic matter, redissolved, transported to deeper water, and concentrated in deep-sea sediments where the content of organic matter is small. Iron is less readily reduced; if
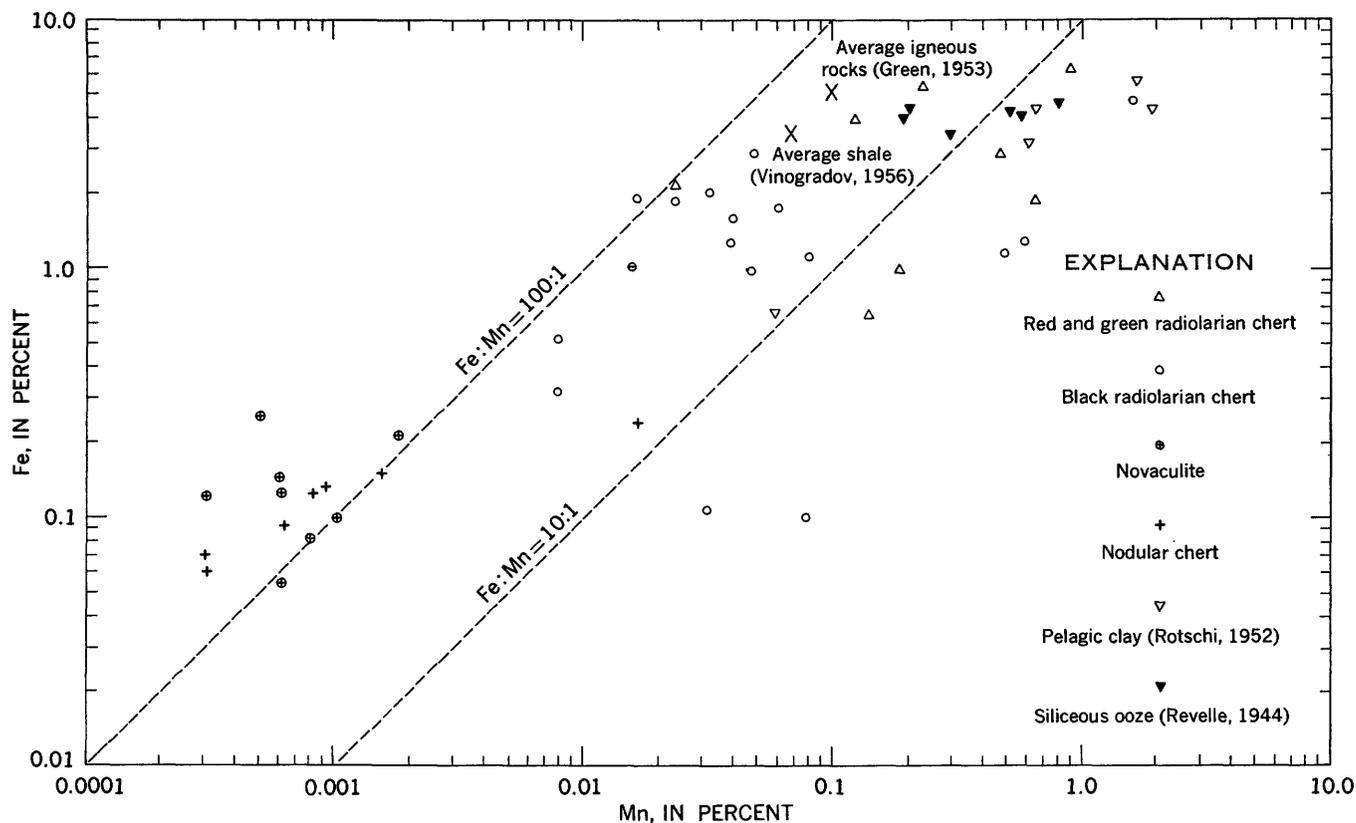
FIGURE 4.—Relation of iron to manganese in chert and related rocks.

reduced, it is more likely to be precipitated as pyrite and is thus deposited more readily in shallow-water sediments. It is therefore surprising that the Fe/Mn ratios of the black and somewhat carbonaceous lydites plotted on figure 4 are not notably higher than those of the radiolarian jaspers; in fact, the average Fe/Mn ratio of the lydites listed in table 4 is only 7.2, considerably lower than 29.8, the average ratio for the radiolarian jaspers in the same table. Planktonic foraminifera are apparently able to extract manganese from sea water (Goldberg and Arrhenius, 1958, p. 195), and manganese may have been added to some black radiolarian sediments in organic remains.

TITANIUM

The relation of TiO_2 to Al_2O_3 in the nondetrital siliceous rocks is shown on figure 5. No marine or lacustrine siliceous sediment is enriched in titanium with respect to either the average igneous rock or the average shale, but the ratio TiO_2/Al_2O_3 ranges widely from that of the average shale, mostly on the side of high titanium. The titanium content of pelagic clay in the oceans has been found to be relatively constant. Arrhenius (1952, p. 31) determined a value of 0.73 percent TiO_2 in pure lutite of the Eastern Pacific which is the same as the TiO_2 content of the average shale (Vinogradov, 1956). High concentrations of titanium in pelagic sediments in-

variably result from the admixture of mafic pyroclastics (Goldberg and Arrhenius, 1958, p. 189; Correns, 1937).

Some of the deviations of the TiO_2/Al_2O_3 ratios of chert from that of the average shale may also be explained by differences in the composition of the admixed clastics. Felsic volcanic ash probably accounts for the low ratios in the black radiolarian chert of Hesse (Hoss, 1957), and many of the radiolarian and diatomaceous cherts in which the ratio is relatively high are associated with and probably contain mafic pyroclastics.

The relatively high TiO_2 content of other cherts cannot be accounted for so easily. The spicular cherts, for example, are certainly not directly associated with volcanics. Kaminskaya (1944) found that many marine organisms concentrate titanium, that plants generally contain more than animals, and that organisms having high calcium, silicon, and iron contents generally also have a higher titanium content, and titanium is apparently concentrated by some siliceous sponges (Bowen and Sutton, 1951) and diatoms (Griel and Robinson, 1952). It is therefore possible that the high TiO_2/Al_2O_3 ratios in the spicular cherts and carbonaceous radiolarian cherts of Thuringia reflect the presence of biogenous titanium. Biogenous titanium
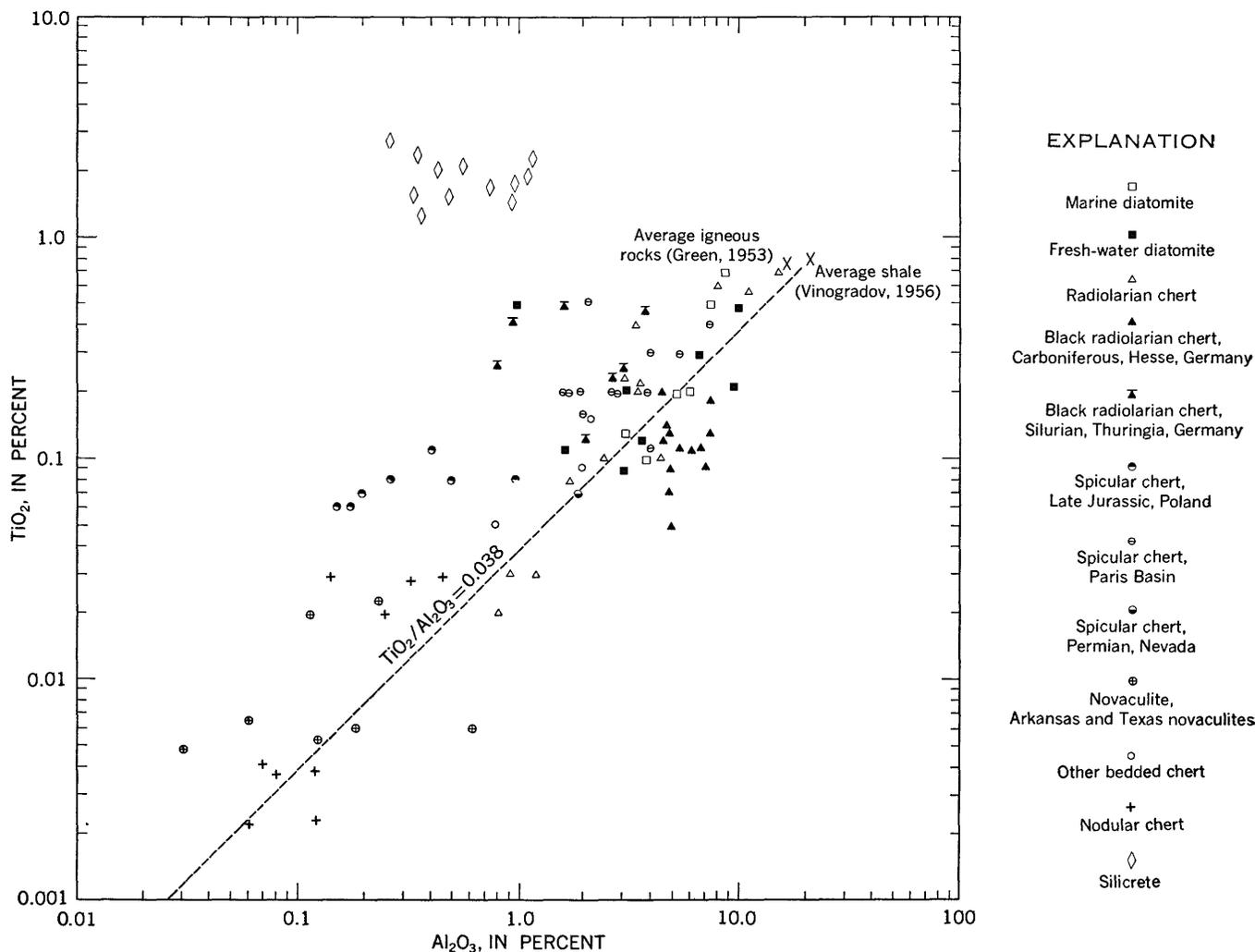
FIGURE 5.—Relation of TiO_2 to Al_2O_3 in chert and related rocks.

might, conceivably, be substituting for silicon in the opaline tests; however, Goldberg (1957, p. 351) suggests that the titanium is scavenged by colloidal iron that is taken up by the organisms.

The higher TiO_2/Al_2O_3 ratio in those nodular cherts with higher Al_2O_3 contents is puzzling, but the number of analyses is too small and the possibility of analytical bias too great to be certain whether or not the differences in the ratio are significant.

Pieruccini (1951b, p. 66) has found the titanium content of chert of Mesozoic age from the Apennines to be of the same order of magnitude as in the associated limestone. The average TiO_2 content of his chert samples is 0.030 percent as compared with 0.044 percent TiO_2 in the limestone. Pieruccini (1951b, p. 70) believes that the titanium is present as orthotitanic acid which is soluable in a weak alkaline solution containing CO_2; thus the titanium content should be low in limestone but high in noncalcareous shale.

The titanium content of silcretes is generally about twice that of the average igneous rock, the average shale, and the clay in which they occur. Most of the titanium is in rutile (Williamson, 1957; Mountain 1952; Frankel, 1952; Frankel and Kent, 1937). The exact manner in which silcretes originate is not known. but they are undoubtedly inorganic and probably can be deposited from either surface or ground waters in areas of tropical weathering (Bassett, 1954; Mountain, 1952; Frankel and Kent, 1937), probably where the water passes from a weathering environment with a pH greater than 9.8 to a less alkaline environment (Siever, 1957, p. 832).

SODIUM AND POTASSIUM

The alkali-metal content is generally high in those siliceous rocks with a high-aluminum content and low in those with a low-aluminum content; most of the potassium and much of the sodium is undoubtedly present

in clay minerals. The median value of the ratio K_2O/Na_2O in sedimentary rocks is approximately 1.7 (Green and Poldevaart, 1958, p. 105) and the average ratio in clay and shale is about 3.1 (Vinogradov, 1956). K_2O exceeds Na_2O in most chert analyses although the ratio ranges widely. In some cherts, however, the Na_2O content nearly equals that of K_2O and in a few analyses actually exceeds it. Relatively high sodium contents in some radiolarian and diatomaceous rocks result from admixed volcanics. This is clearly shown in analyses of radiolarian cherts of Carboniferous age of Hesse (Hoss, 1957); sodium is the dominant alkali metal of tuffaceous chert in which it is present in albite, but potassium is more abundant in those cherts with little or no volcanic component. In some diatomaceous rocks, the sodium may be an exchangeable base in an alumina-ferric oxide-silica gel (Robertson and Twedily, 1953). No explanation has been advanced to explain the low K_2O/Na_2O ratios in some spicular and nodular cherts, but they may result from the presence of authigenic albite or, in the opaline rocks, from the presence of sodium in the interstices of the tridymite lattice. Whatever the explanation, the sodium content does not seem greater than in many carbonate rocks.

TRACE ELEMENTS

Few cherts have been analyzed for trace elements. The analyses that are available (table 10) indicate that although certain cherts are enriched in some trace elements with respect to the average igneous rock, the enrichment can generally be ascribed to the admixed material.

The only cherts showing clear evidence of enrichment are the black cherts. At least some of the black radiolarian cherts are enriched in copper, molybdenum, nickel, lead, and vanadium, and the black chert sample from the Maravillas Chert may be slightly enriched in arsenic. The samples showing the most enrichment are those from Thuringia which are also the most carbonaceous. All these elements are commonly enriched in black shales (Krauskopf, 1955), so their enrichment in black chert probably results from the presence of organic matter. The form in which these metals occur is not known. Some may be present as metal-organic compounds (Krauskopf, 1955, p. 421); the vanadium may occur in clay minerals or micas (W. W. Rubey, quoted in Krauskopf, 1955, p. 421) or in the iron oxide minerals (Hoss, 1957, p. 71).

The trace-element content of radiolarities from three localities in Switzerland were determined by semiquantitative methods by Grunau and Hügi (1957). One group of samples was enriched in chromium and titanium, another group was chromium-free and titanium-poor, and the third was enriched in copper, lead, and strontium. The chromium and titanium in the first group were thought to be caused by the presence of clastic serpentine and peridotite particles which were also thought to be the cause of the green color of the chert.

Giannini and associates (1950) found the Ni/Co ratio to average 0.37 in chert nodules of Mesozoic age from the Apennines and 0.52 in the surrounding limestone as compared to 2.5 or even 10 or 20 in eruptive rocks. They interpret the lower ratio in limestone and chert as resulting from the activity of organisms that require cobalt in metabolism.

ISOTOPIC COMPOSITION

SILICON

The relative abundances of Si^{28} and Si^{30} have been investigated by Marsden (in Rankama, 1954), Reynolds

TABLE 10.—*Trace-element content of chert in parts per million*

Element	Igneous rocks [1]	Sand-stone [2]	Lime-stone [2]	Shale [3]	Radiolarian chert								Other bedded chert				Nodular chert in carbonate rock [7]	
					Black		Black tuffaceous		Black	Red		Pre-cambrian, Minn.[6]	Upper Ordo-vician, Texas [6]	Arkansas and Caballos Novaculites [7]				
					Carboniferous, Germany [4]		Carboniferous, Germany [4]		Carbon-iferous, Ger-many [5]	Jurassic, Cali-fornia [6]								
					Aver-age	Max-imum	Aver-age	Max-imum						Aver-age	Max-imum	Aver-age	Max-imum	
As	2	1	1	[6] 10							0.5	0.6	10.1	0.8	1.0	1.0	1.6
Co	25	.3	.2	[8] 20	15	20	25	30									
Cr	120	35	11	[9] 90													
Cu	60	10-20	5	50	80	150	>150	150	150								
Ga	18	12	4	20													
Ge	1-2	1-2	.2	2							.9	.7	.0	.4	1.5	.3	2.0
La	40	30	1-10	40-90													
Li	40	15	5	60							26	8	9	3.0	13	20	36
Mo	1-2	<1	0.1-0.5	[8] 2							4.4	3.2	11.4	1.0	3.0	2.4	3.4
Ni	60	2	10	[8] 70	100	180	80	160	210								
Pb	16	7	10	[9] 20													
V	30	10-20	20	[8] 130	165	270	670	970	1,100								
Zn	80	12	4	90													
Zr	170	200?	20?	160													

[1] Green, 1953, and Fleischer, written communication, 1960.
[2] Krauskopf, 1955, p. 416; Pettijohn, written communication, 1960 (sandstone); Turekian and Wedepohl, 1961.
[3] Vinogradov, 1956, Krauskopf, 1955; Turekian and Wedepohl, 1961.
[4] Hoss, 1957.
[5] Hoss, 1957, 1 sample.
[6] Maxwell, 1953, 1 sample.
[7] Maxwell, 1953, 7 samples.
[8] Enriched in black shale.
[9] Possibly enriched in black shale (Krauskopf, 1955, p. 420).

and Verhoogen (1953), and Allenby (1954), and the results are summarized and discussed by Rankama (1954, p. 273). Most of the available data for the nondetrital siliceous sediments are listed in table 11; inasmuch as the different investigators used different standards, their results are not strictly comparable (Rankama, 1954, p. 273) and are therefore listed in separate columns.

TABLE 11.—*Relative abundance of Si isotopes in nonfragmental siliceous sedimentary rocks*

	Marsden, in Rankama, 1954 (Si^{28}/Si^{30})	Allenby, 1954 (Si^{28}/Si^{30})	Reynolds and Verhoogen, 1953 (δ) [1]
Water, Lake Windermere, England	29.34		
Diatom, Lake Windermere, England	29.55		
Do	29.56		
Diatomite, Kentmere, England	29.59		
Diatomite, North Ireland	29.48		
Diatomite, fresh water, California			−1.6
Diatomaceous chert, California			+.5
Radiolarite, Barbados	29.54		
Do		29.73	
Radiolarian chert, California			+1.0
Flint, Dover Chalk, England			−1.8
Silicified wood	29.41		
Do	29.50		
Siliceous sinter, Yellowstone Park		30.10	
Do			−2.1
Quartz, Precambrian	29.21		
Basalt, Hawaii		30.02	
Quartz from pegmatite, Ontario		29.86	
Quartz from pegmatite, California			−.1
Vein quartz, Arkansas			−1.1
St. Peter Sandstone, Wisconsin			−1.1

[1] $\delta = 100 \cdot \dfrac{(Si^{30}/Si^{28}) - (Si^{30}/Si^{28})O}{(Si^{30}/Si^{28})O}$ where $(Si^{30}/Si^{28})O$ is the ratio in an olivine standard.

In a theoretical discussion of the partition of silicon isotopes, Grant (1954, p. 240) concluded that heavier isotopes should favor the precipitated phase and that silica precipitated from aqueous solutions either organically or inorganically should therefore contain concentrations of Si^{30}. The results of Allenby and Reynolds and Verhoogen indicate that marine accumulations of siliceous organisms are enriched in Si^{30}, which is in accord with Grant's conclusion, but Reynolds and Verhoogen (1953, p. 233) attribute the concentration to selective organic processes. However, Marsden's data from Lake Windermere indicate that at least one genus of diatoms concentrates the lighter isotope. Reynolds and Verhoogen (1953, p. 233) believe the enrichment of the fresh-water diatomite in Si^{28} may have resulted from a volcanic source of the silica and cite the isotope ratio in siliceous sinter as supporting evidence. If their conclusion is correct, the marked enrichment of the one analyzed sample of radiolarian chert from the Franciscan Formation in Si^{30} is of considerable interest inasmuch as the silica in the Franciscan has generally been ascribed to a volcanic source. The enrichment of the flint from the Dover chalk in Si^{28} is anomalous and Reynolds and Verhoogen did not attempt an explanation. The equilibrium constant of the isotope-exchange re-

action is a function of temperature, and silica deposited from cool water might be expected to contain a higher proportion of Si^{30} than silica deposited from warm water, but the few data and the uncertainty as to the isotopic composition of the liquid phase preclude any evaluation of the temperature effect.

OXYGEN

The O^{18}/O^{16} ratio has been determined for a few samples of chert and diatomite by Baertschi (1950), Silverman (1951), Clayton and Epstein (1958), and Engel, Clayton, and Epstein (1958). Their results are listed in table 12 along with a few determinations of the ratio in quartz from igneous rocks; the standard for all determinations is Hawaiian sea water [6]. The concentration of O^{18} in the siliceous sediments is evident. The oxygen-isotope ratio in silica precipitated from marine water might be expected to vary in the same manner as the ratio in carbonates (that is, O^{18} would be more concentrated in silica deposited from cold water than warm water), but a silica-oxygen temperature scale has not been worked out for the range of temperatures in the marine environment, and it may not be possible to do so (Urey and others, 1951, p. 402).

Hydrothermal alteration decreases the O^{18}/O^{16} ratio; thus Engel and others (1958) found that in chert occuring in the unaltered Leadville Limestone of Mississippian age, δ ranged from 28.0 to 29.4 whereas in chert from hydrothermally altered areas δ ranged from 22.2 to 24.2. Metamorphism also decreases the ratio (H. L. James, oral communication, 1958).

TABLE 12.—*Relative abundance of oxygen isotopes in nonfragmental siliceous sedimentary rocks*

Sample	δ [1]
1. Hard black chert in chalk; Cretaceous, France [2]	34.1
2. Diatomite [3]	30.3
3. Dark-gray chert; Mississippian, Colorado [4]	29.4
4. Dark-gray chert nodule; Mississippian, Colorado [4]	29.4
5. Flint, Dover Chalk [3]	29.3
6. Black chert in fine-grained limestone; Mississippian, Colorado [2]	29.2
7. Medium-gray chert nodule; Mississippian, Colorado [4]	28.6
8. Chert bed; Mississippian, Colorado [4]	28.0
9. Quartz from leucogranite; California [2]	10.4
10. Quartz from granodiorite; California [2]	9.6
11. Quartz from granodiorite; New Mexico [2]	8.9

[1] $\delta = \left(\dfrac{R \text{ (sample)}}{R \text{ (standard)}} - 1 \right) 1{,}000$, where $R = \dfrac{O^{18}}{O^{16}}$

[2] Clayton and Epstein, 1958.
[3] Silverman, 1951.
[4] Engel and others, 1958.

SOLUBILITY OF SILICA AT LOW TEMPERATURES

Reliable experimental determinations of the solubility of quartz at room temperatures have not been made, but the extrapolation of Kennedy's (1944) curves for the solubility of quartz under hydrothermal conditions indicates extremely low solubilities at tempera-

[6] The Hawaiian sea water has a $\delta = 0.2$ relative to mean ocean water (Clayton and Epstein, 1958, p. 359).

tures prevailing at the surface of the earth. Thermodynamic calculations of Siever (1957, p. 825) yielded results of 7.25 and 14 parts per million for the solubility of quartz in pure water at 25°C. Although many surface waters are undoubtedly supersaturated with respect to quartz, the attainment of equilibrium is very slow, and no direct evidence exists that quartz is precipitated directly from waters in the sedimentary environment except during diagenesis (Siever, 1957, p. 834).

The amount of SiO_2 dissolved from amorphous silica in pure water is 60 to 80 ppm at 0°C, 100 to 140 ppm at 25°C, and 300 to 380 ppm at 90°C (Krauskopf, 1956, p. 23; Okamoto and others, 1957, p. 125, determined solubilities about 50 to 70 percent greater than those of Krauskopf). Below about pH 9 the dissolved silica is nearly all in the form of monosilicic acid, H_4SiO_4 and the solubility is little affected by changes of pH, but above pH 9 the solubility increases rapidly as the alkalinity increases (Krauskopf, 1956, p. 23). The amount dissolved is about the same in artifical sea water as in fresh water (Krauskopf, 1956, p. 24). Bruevich (1953) concluded from the average maximum silica content of interstitial waters in unconsolidated sediments that the solubility of silica in sea water is about 70 parts per million, which agrees fairly well with Krauskopf's experimental results.

The apparent solubility of silica in water is greatly reduced by the addition of either aluminum oxide or powdered aluminum, probably by the formation of an insoluble aluminum silicate on the surface of the silica phase (Iler, 1955, p. 14). Okamoto and others (1957, p. 130) report that the addition of aluminum sulfate also reduces the solubility of silica with the greatest reduction in solubility for a given amount of aluminum being between pH 8 and 9.

The oceans and nearly all rivers contain much less silica than the saturation values determined in the laboratory for amorphous silica, the maximum content reported in the oceans being 26.7 ppm SiO_2 (Bruevich, 1953), so direct inorganic precipitation of silica should not be expected. However, Bien and others (1958) have found that most of the dissolved silica in Mississippi River waters is precipitated, mostly by inorganic processes, when the river water mixes with water of the Gulf of Mexico. Bien and his coworkers conclude that the process is largely an adsorption of soluble silica on suspended matter as it comes in contact with electrolytes of the Gulf water, although some is probably removed by co-precipitation with aluminum ions.

ORIGIN

The very common association of deposits of siliceous organisms, particularly diatoms, with volcanic ash has been noted by many authors (Bramlette, 1946, p. 39). This association has led Taliaferro (1933, p. 54) and Bramlette (1946, p. 41) among others to suggest that much of the silica and perhaps much of the other nutrients utilized by the organisms may have been released by the weathering of volcanic ash. Trask (1932, p. 237) emphasizes the necessity of adequate nitrate for high organic activity, as in areas of turbulence or upwelling (Harvey, 1955, p. 99–101). Much of the nitrate and phosphate must thus be available through the cycle of renewal and upwelling, but unusual supplies of silica from the volcanics might be critical for long-continued extraction of silica that is being permanently removed as the opaline tests of diatoms (Bramlette, written communication, 1958).

In addition to extracting soluble silica from water, some diatoms are capable of obtaining silica directly from aluminosilicate minerals (Murray and Irvine, 1889; Hutchinson, 1957, p. 790). Gawel (1950) has noted that cherts (mostly radiolarian) in the Flysch of the Carpathians occur in argillaceous parts of the sequence but are uncommon in the more calcareous parts; he concludes that the siliceous organisms derived their silica from clays and that their growth was favored by periods of argillaceous deposition.

The apparently inorganic silica in bedded chert has undoubtedly formed in several different ways, but the relative importance of the different sources and processes cannot be assessed. Bramlette (1946, p. 50–52) has shown that much matrix silica in the Monterey Formation has resulted from the solution, migration, and redeposition of the silica in diatom frustules. Arrhenius (1952, p. 85) has found such a process operative in some sediments of the East Pacific, and Sujkowski (1932, 1933b) has presented convincing evidence for a similar origin of matrix silica in radiolarian cherts of Poland. The common association of black shale and bedded chert indicates that many cherts such as the Fort Payne Chert that show no direct evidence of organic origin were deposited in areas of high organic activity and suggests that they may have resulted from the reorganization of organic silica.

Silica in bedded chert and siliceous shale can also be derived from the alteration of volcanic ash (Bramlette, 1946, p. 44; Rubey, 1928, p. 168–169), probably during the early stages of diagenesis. Such a process may have been of great importance in the formation of chert from tuffaceous eugeosynclinal sediments such as those of the Paleozoic of central and western Nevada (R. J. Roberts, oral communications, 1959).

Inasmuch as sea water is undersaturated with respect to amorphous silica, the hypothesis of the origin of bedded chert by direct precipitation seems no longer

tenable except locally in areas of volcanism (Krauskopf, 1956, p. 25). If the silica content of sea water is governed by a combination of adsorption processes and organic extraction, the silica content of the water may have varied widely through geologic time, particularly in response to evolutionary development of siliceous organisms.[7] Siever (1957, p. 838) believes that radiolaria and sponges, and later diatoms, were able to hold down the silica concentrations in sea water sufficiently to prevent inorganic precipitation, at least from Paleozoic time on, basing his conclusion on the similarity of Paleozoic cherts to those of more recent geologic age. Inorganic precipitation may have been operative on a a larger scale in the Precambrian before evolution of the radiolaria (see also Kaleda, 1956).

The common association of radiolarian chert with volcanic rocks has led many investigators to conclude that silica was supplied either by the volcanics themselves (Krauskopf, 1957, p. 75) or by associated siliceous springs (Davis, 1918, p. 402) in amounts exceeding the solubility of amorphous silica in normal sea water. As the thermal waters would cool, the silica would be precipitated inorganically; any included radiolaria would be incidental. Stephens (1956, p. 305) has proposed a slight modification of the theory to account for chert of Paleocene and Eocene age in Borneo. He proposes a volcanic source, but cites evidence to indicate that the chert resulted from post-depositional silicification of argillaceous sediments.

The close association of radiolarian chert and lava flows such as that in the Franciscan Formation of California (Taliaferro and Hudson, 1943) does strongly suggest a volcanic source for the silica, but the association does not in itself prove it. The function of the flows might have been merely the establishing of a marked thermal gradient which would facilitate solution, migration, and redeposition of disseminated silica in the sediment.

There is general, but by no means universal, agreement that nodular cherts in carbonate rock were formed by replacement of the host carbonate rock (Pettijohn, 1957, p. 439). Certainly many chert nodules exhibit definite evidence of origin by replacement, but the field and petrographic evidence is inconclusive for many and perhaps most occurrences; the principal evidence against origin of these nodules by primary precipita-

tion is the recent experimental evidence indicating that sea water is undersaturated with silica.

According to Chilingar (1956), limestones with a high concentration of chert nodules and stringers generally have high Ca/Mg ratios, indicating that the high pH and temperatures that favor the deposition of dolomitic limestone do not favor the precipitation of chert. If the Ca/Mg ratio is higher in the chert bands than in the adjacent limestone bands, Chilingar interprets the cherts as probably being primary.

Giannini and others (1950) explain chert bands and layers of nodules in limestone of the central Apennines as having resulted from periodic solution of calcium carbonate from an original uniform siliceous-calcareous sediment, and Dunbar and Rodgers (1957, p. 248) describe light-colored vitreous chert that has resulted from the weathering of a dolomite containing 20 percent of finely divided silica.

Organic skeletal remains disseminated through the sediment were an adequate source of silica for some occurrences of nodular chert (Lowenstam, 1942b; Andrusov, 1932; Richardson, 1919, p. 539). For others, the paucity of siliceous organisms in either the chert or the surrounding rock has been taken as strong evidence of an inorganic source (Biggs, 1957). The recent investigation of Bien and coworkers (1958) indicates that much inorganically precipitated silica is disseminated through sediments and would be available for redistribution, but most such silica would be in argillaceous deltaic sediments, an environment in which both bedded and nodular cherts are uncommon.

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[7] Of the major silica-secreting organisms, sponges are known from the latest Precambrian, radiolarians from the earliest Paleozoic and possibly from the Precambrian, diatoms from the early Mesozoic, and silicoflagellates from the Late Cretaceous. According to Vinogradov (1953), siliceous sponges became less important during the middle Paleozoic when calcareous sponges evolved; yet spicular cherts of considerable thickness and extent are known in rocks of late Paleozoic, Mesozoic, and Tertiary age.

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