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Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks

Part IV-A

Isotopic Composition Chemical Analyses

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GEOCHEMISTRY OF CARBONATE SEDIMENTS AND SEDIMENTARY CARBONATE ROCKS

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FOREWORD

Detailed knowledge of the chemical and mineralogical variations that exist in the carbonate rocks limestone and dolomite and of the processes responsible for this diversity is fundamental to the Illinois State Geological Survey's program of furthering the practical utilization of these natural resources of Illinois. Chemical composition is particularly important when the rocks are used as agricultural limestone and fluxing stone or in the manufacture of dolomite refractories, lime, calcium carbide, sodium carbonate, glass, and other products.

The invitation extended to Dr. Graf by the United States Geological Survey to prepare the chapter on sedimentary carbonates for their revision of F. W. Clarke's "Data of Geochemistry" has afforded a valuable opportunity for the state and federal geological surveys to cooperate in a basic review of selected topics in carbonate geochemistry. The resultant material is presented in a series of Illinois State Geological Survey Circulars and subsequently will serve as the basis for a condensed treatment in the revised "Data of Geochemistry."

Part I, published as Circular 297, includes an introduction and sections on carbonate mineralogy and carbonate sediments.

Part II, Circular 298, presents the section on sedimentary carbonate rocks.

Part III, Circular 301, deals with the distribution of minor elements.

Part IV-A, Circular 308, discusses isotopic composition and presents chemical analyses. Part IV-B, Circular 309, contains the bibliography for the first four parts.

Part V, concerned with aqueous carbonate systems, will be published with its own bibliography at a later date.

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ABSTRACT

The distribution of major and minor elements in sedimentary carbonate rocks and the mechanisms responsible for this distribution are considered on the basis of published information contained in geologic studies, and in studies of present-day environments of carbonate deposition, isotopic composition of carbonates, and experimental aqueous and nonaqueous carbonate systems.

Part IV-A presents chemical analyses and discusses isotopic composition.

ISOTOPIC COMPOSITION

OXYGEN ISOTOPES

The relative abundances of the three stable oxygen isotopes, O^{16}, O^{17}, and O^{18}, vary in nature by as much as 10 percent; in air they occur in the proportion 99.759 : 0.0374 : 0.2039 (Nier, 1950; Epstein, 1959). Craig (1957b) adopted a value for 10^5 $(O^{16}O^{18}/O^{16}O^{16})$ of 413.97 for CO_2 produced by reaction of 100 percent H_3PO_4 with the sample of Solenhofen Limestone on which Nier earlier measured precise isotopic abundance ratios. The National Bureau of Standards Solenhofen Limestone standard (No. 20) gives a value of 414.08.

The fractionation factor of particular interest in carbonate precipitation is that for the reaction

$$H_2O^{18}\ (l) + 1/3\ CaCO_3{}^{16}(s) \rightleftharpoons H_2O^{16}\ (l) + 1/3\ CaCO_3{}^{18}(s)$$

Urey (1947), using a model that ignored the potential fields in the crystal, calculated the equilibrium constant K = 1.0220 at 0° C and 1.0176 at 25° C. These values represent a -5.7° C change in temperature for 1‰ increase in O^{18}/O^{16}. McCrea (1950) obtained theoretical values of 1.0255, 1.0206, and -5.1 by including estimates of the effects of translational and hindered rotational degrees of freedom in the solid state. Equilibrium constants such as these, calculated from a theory for gases but applied to reactions involving condensed phases, must of necessity be of limited accuracy. Epstein et al. (1953) experimentally obtained -4.3° C/mil for present-day shells, a value in satisfactory agreement with McCrea's (1950) earlier experimental determination for inorganically precipitated $CaCO_3$.

Epstein (1959) stated that the fractionation factor in the $CaCO_3$-H_2O system has been shown to be independent of pH, of the relative amount of each phase, of the polymorphic form of $CaCO_3$ being precipitated, of whether fresh or sea water is involved (ionic strength), and apparently of pressure and of small amounts of Mg and Sr in the calcite structure. Laboratory experiments by McCrea (1950) and by Lowenstam and Epstein (1957) show that it is difficult to precipitate $CaCO_3$ rapidly enough from supersaturated but dilute solutions at the pH of ocean water so that oxygen isotope equilibrium is not attained.

Clayton (1959) experimentally determined equilibrium constants in the temperature range 190° to 750° C for the calcium carbonate — water oxygen isotope exchange reaction, and in the range 9° to 19° C he computed them from the data of Epstein et al. (1953). Both sets of data fit very well the straight line described by

$$\ln K = 2725\ T^{-2}$$

for which the equilibrium constant at 25° C is 1.03187. The times required for isotopic equilibration, starting with aragonite and adding NH_4Cl to increase $CaCO_3$ solubility, lay between 100 and 1000 hours in Clayton's experiments.

The oxygen isotopic composition of carbonate materials assembled in table 1 are expressed in permil units of δO^{18}, where δO^{18} is equal to

$$1000 \left(\frac{(O^{18}/O^{16}\ \text{sample}) - (O^{18}/O^{16}\ \text{standard})}{(O^{18}/O^{16}\ \text{standard})} \right)$$

Measurements from other laboratories, whenever possible, have been referred to the Chicago PDB standard (see Craig, 1957b). Some of the earlier results not included in this review were discussed by Ingerson (1953).

The δO^{18} values for modern marine shells deposited in the temperature range 0° to 30° C in sea water of mean composition should range from about +1.5 to -3.0‰, according to the temperature dependence defined by Epstein et al. (1953), and this is generally true (table 1). The δO^{18} values are of course affected by anything that changes the oxygen isotopic composition of sea water, such as the influx of fresh water from rivers and the addition of low-O^{18} water from the melting ice at high latitudes. Evaporation and condensation processes affect both the O^{18}/O^{16} ratio of sea water and its salinity, so that there is a correlation, assumed to be linear (Epstein et al., 1951), between these two variables. In a nonglacial period, the expectable marine salinity variation from 33 to 37‰ would result in a corresponding δO^{18} variation in $CaCO_3$ of 0.6 to 0.8‰, corresponding to 3° or 4° C (Lowenstam and Epstein, 1954). Possible changes in the isotopic composition of sea water with geologic time have thus far been ignored, and the effect upon the large oceanic reservoir of precipitation of relatively small amounts of carbonates can be shown to be negligible.

The observed δO^{18} values for modern shells are also a function of two variables peculiar to living organisms. Some organisms deposit $CaCO_3$ in only a portion of the total annual temperature range, and the mean δO^{18} values for these shells are thus not those corresponding to the mean annual temperature (see Urey et al., 1951; Epstein and Lowenstam, 1953; Lowenstam and Epstein, 1954). The majority of the pelecypods examined by Epstein and Lowenstam at Bermuda seemed to grow primarily during periods of warm temperature, whereas all but one of the gastropod species seemed to show winter as well as summer growth. Some forms like *Pinctada radiata* include shell grown at low temperatures, whereas sessile foraminifera at Bermuda grow at very warm temperatures. *Chama macerophylla* lays down shell material only at temperatures above 21° C, although the annual water temperature range is 18° to 29° C.

Epstein et al. (1953) found that shells grown in sea water maintained at constant temperature were deposited in oxygen isotopic equilibrium with the water without any observable isotopic anomalies resulting from differences in the rate of animal metabolism. However, there is also evidence that some organisms deposit $CaCO_3$ out of equilibrium with the surrounding water. Lowenstam and Epstein (1957) showed that some of the algal carbonates from the Bahamas that they examined, for which depositional temperatures from 22.8° to 39.8° C are indicated by the δO^{18} values, must have formed out of equilibrium with the surrounding waters because the maximum temperature of the water is about 30° C. The mean temperature calculated for a number of samples of oolites from the same area is, by comparison, in relatively good agreement with the observed mean annual temperature. Present-day shoal-water coelenterates and echinoderms also apparently deposit $CaCO_3$ out of isotopic equilibrium, although Lowenstam and Epstein (1954) suggested that the measurements for the echinoids might be in error because of failure to remove all of the finely divided organic matter.

Urey et al. (1951) noted that marine animals do not maintain body temperatures above that of the sea, so that the relationships discussed thus far are not complicated by this additional factor. These relationships would not, however, be expected to hold for air-breathing animals.

The oxygen isotopic composition of shells and of carbonates in general may be altered after their formation by reactions involving isotopic exchange with water, such as dolomitization, aragonite-calcite transformation, and simple recrystallization of calcite, as well as by solid state diffusion. Urey et al. (1951) considered solid state diffusion and calculated that a crystal one millimeter on a side should retain 96.4 percent of its original concentration for $7x10^8$ years at 20° C, or $6.4x10^4$ years at 100° C, relative to the equilibrium of a changed environment. The best indication of the preservation of original δO^{18} values is the persistence of systematic zonal variations of isotopic composition in shells, corresponding to seasonal temperature variations of the water in which the organisms lived. Belemnites, which are made up of large, closely fitted calcite crystals, have in some cases retained their original oxygen isotopic composition since Jurassic time (Urey et al., 1951).

The temperature dependence of the O^{18}/O^{16} ratio has been used to measure paleotemperatures, a subject not under consideration here. Such O^{18}/O^{16} data are also of interest, however, as a measure of the range of isotopic compositions present in carbonate fossils and as a guide to the processes that went on in environments of carbonate deposition.

Emiliani in a series of papers (1955a, 1955b, 1956) reported on the oxygen isotopic composition of various species of pelagic foraminifera concentrated from *Globigerina* oozes encountered in Mediterranean and deep sea cores. The over-all δO^{18} range for several hundred such samples from the Pleistocene of the Atlantic and Pacific Oceans, +1.92 to -2.10, reflects the somewhat different depth-temperature zones in which the various species lived, variations in isotopic composition of the water, and periodic Pleistocene oscillations of about 6° C in Atlantic surface ocean temperatures. Shorter ranges corresponding to more restricted temperature variations are shown by pelagic foraminifera of Pleistocene age from the Mediterranean, and those of Oligocene and Miocene age from the equatorial and subtropical Atlantic Ocean. Average δO^{18} values for Atlantic and Pacific benthonic foraminifera of Pleistocene age are included in table 1.

In an extensive study of Upper Cretaceous fossils, principally from western Europe and the southeastern United States, Lowenstam and Epstein (1954) found that carefully selected brachiopods and pelecypods (genus *Inoceramus*), as well as belemnites and a few polychaete worm tubes and scaphopods examined, gave reasonable temperatures indicating probable preservation of original δO^{18} contents. The brachiopods were noteworthy in giving δO^{18} values from 0.6 to 1.3‰ lower than those of the belemnites, but paralleling the variation of δO^{18} values of the belemnites with time. This relation was believed by Lowenstam and Epstein to be indicative of local bottom climates in which the brachiopods lived. Conversely, the parallelism of the brachiopod and belemnite values indicated that the belemnites give isotopic records of shelf seas, rather than of wide ranging migration routes. The over-all consistency of the belemnite data was shown by similar temperatures over a large area, with a latitudinal climatic gradient from the Gulf Coast of the United States to Scandinavia that is detectable for at least Maestrichian time. Many of the oyster shells, which are quite porous, would appear to have been infiltrated by later O^{18}-poor calcite deposited from fresh water. The enclosing chalks showed an unusually wide range of δO^{18} values and a mean δO^{18} value above that of the several fossil groups, a not improbable result, according to Lowenstam and Epstein, for variable mixtures of bioclastic debris supposedly consisting largely of the tests of planktonic organisms. Some of the chalks that have δO^{18} values corresponding to temperatures greater than 30° C would appear, however, to contain some light $CaCO_3$ introduced after original deposition.

The existence of a temperature threshold for pelecypods but not for gastropods, described above for present-day forms at Bermuda, also is indicated by the higher δO^{18} values for gastropods relative to pelecypods in an assemblage of well preserved aragonitic fossils from the Upper Cretaceous Coon Creek Tongue of the Ripley Formation in western Tennessee (Lowenstam and Epstein, 1954).

The interpretation of δO^{18} anomalies in fossil materials is thus seen to be an exceedingly complex problem, involving as it does consideration of secondary infiltration and possible equilibration with nonmarine waters, different temperature thresholds for growth, different temperatures of formation, possible migration of the organisms during life, variations in the isotopic composition of sea water resulting, for example, from influxes of glacial meltwater, and possible precipitation of organic $CaCO_3$ out of isotopic equilibrium.

Ocean waters rarely vary in δO^{18} by more than 2‰. Fresh waters are variably depleted in O^{18} relative to ocean water, depending upon latitude and altitude, because of fractionation of oxygen isotopes during evaporation (Epstein and Mayeda, 1953). The variable O^{18} depletion is reflected in the variable isotopic composition of modern fresh-water carbonates (Baertschi, 1957; Clayton and Degens, 1959; table 1). The very light $CaCO_3$ deposit at the Pfäfer spring is said by Baertschi to have formed on the walls of the spring shaft, where thermal vapor with δO^{18} = -22.5 (relative to the Chicago standard) regularly condenses. The two Miocene nonmarine limestones from Idaho (table 1) apparently were deposited in a lake at high elevation, and they seem to have retained their original isotopic composition.

The work of Clayton and Degens (1959) indicated that Paleozoic marine limestones have typically undergone oxygen isotopic exchange with post-depositional fluids of lower O^{18} content until these limestones hardly differ from nonmarine limestones in oxygen isotopic composition. Baertschi (1957) likewise found that virtually all of the nonmetamorphosed marine limestones he examined had δO^{18} values lower than those expectable for normal marine precipitation. Comparisons of the isotopic compositions of secondary calcite veinlets with those of the host (table 1) clearly illustrate the effect of such later infiltration. Samples from the marine Leadville Limestone of Mississippian age, in areas unaffected by hydrothermal activity, gave δO^{18} values that rather uniformly differ by about -6‰

from those for carbonate laid down in isotopic equilibrium with sea water (Engel et al., 1958). The difference and the uniformity of values suggested to Engel et al. that there had been extensive post-lithification isotopic exchange with connate or ground waters.

The extent to which the oxygen isotopic composition of limestones will be altered by metamorphic or hydrothermal activity depends upon the volume of heated fluid associated with the process, as well as on the temperature and isotopic composition of the fluid, and it is possible for recrystallization to occur with very little change in isotopic composition (see range of δO^{18} values for metamorphic carbonate rocks given by Baertschi, 1957). In the Leadville area, Colorado, the transition between isotopically unaltered limestone and that altered by hydrothermal activity is very sharp. Engel et al. (1958) found O^{18} contents below the typical value for sedimentary limestone only in samples showing visual evidence of recrystallization. Limestone an eighth of an inch from the contact with a quartz-latite sill, or a few inches from narrow veins of hydrothermal dolomite and weak sulfide mineralization, had essentially the same isotopic composition as samples a thousand feet away.

The temperature dependence of the oxygen isotope fractionation between quartz and calcite in isotopic equilibrium has not yet been measured in laboratory experiments. However, Clayton and Epstein (1958) have outlined this relationship from measurements of natural samples that are believed to have formed in equilibrium with large volumes of isotopically similar water and that therefore yield a straight line on a δ_{quartz} versus $\delta_{calcite}$ plot. Several pairs of quartz and calcite samples from vugs that from geologic evidence appear to have formed at different times have isotopic compositions indicating that they are not equilibrium pairs. The difference in isotopic composition of the calcite and quartz decreases with increasing temperature, and is thus at a maximum for sedimentary materials (table 1). Comparable data for dolomite-quartz pairs plotted on a δ_{quartz} versus $\delta_{dolomite}$ diagram fall on a straight line with a slope of unity, indicating no isotopic fractionation between the oxygen in these two minerals. Thus the isotopic fractionation between calcite-dolomite mineral pairs must be temperature dependent, although no measurements have yet been published.

Isotopic analysis of a single mineral from a specific locality usually does not show that the mineral was in isotopic equilibrium with its surroundings when it was recrystallized (Engel et al., 1958), and thus isotopic examination of mineral pairs is highly desirable in the making of temperature estimates. Engel et al. found that,in the Leadville area studied, δO^{18} values from single minerals had considerable significance. Nevertheless the differentiation between diagenetic and hydrothermal recrystallization of limestone that they were able to make using quartz-calcite pairs would not have been possible with, for example, calcite alone, because reaction with heated solutions and with nonmarine diagenetic solutions or ground water would both have resulted in decrease of δO^{18} relative to that of marine carbonate.

CARBON-14

The radioactive isotope C^{14}, with a half-life of 5568 ± 30 years (Libby, 1955) is formed in the upper atmosphere by reaction between neutrons and N^{14}, after which it quickly reacts with oxygen to form $C^{14}O_2$. Although the cosmic ray neutron component is some 3.5 times greater in polar than equatorial regions (Simpson, 1948; Yuan, 1949), the effectiveness of atmospheric mixing is shown by the fact that samples from various points on the earth's surface and in the atmosphere agree within the statistical error of measurement (Libby, 1955). This error, given by Libby as some 3 to 5 percent, is now said by Brannon et al. (1957) to be less than 1 percent for contemporary concentrations of C^{14}.

Libby found no evidence that the intensity of cosmic radiation or the composition of the carbon reservoir, predominantly contained in the oceans, has changed significantly in the last 20,000 or 30,000 years. More recent evidence has been cited by deVries (1959) for believing that there may be shorter term fluctuations in neutron flux as a result of solar activity. Craig (1954b) had earlier concluded from measurements of the C^{13} content of Sequoia growth rings that the isotopic composition of atmospheric carbon had been constant to at least 1‰ from 1072 B.C. to 1649 A.D., and that irregular 1‰ variations with a rough periodicity of about 400 years were more probably due to the effects of varying external conditions on the assimilation and respiratory processes of the tree than to atmospheric changes.

Carbonate materials as encountered today should therefore to a first approximation have a C^{14} content that is simply the fixed percentage originally incorporated by precipitation in equilibrium with the carbon reservoir, minus that lost since precipitation by decay of C^{14}. With present isotopic enrichment procedures (Haring et al., 1958), measurements of C^{14} content have been attempted on materials as much as 70,000 years old.

Table 2, reproduced from Libby's book (1955), gives the C^{14} content of modern shells. The average of these few measurements is 15.9 absolute disintegrations per minute per gram. A value of 16.1 Dpm/g may be calculated from the average Dpm/g of 15.3 ± 0.1 for samples from the terrestrial biosphere and the ratio

$$\frac{C^{13}_{\text{inorganic C}}}{C^{13}_{\text{biological C}}} = 1.025$$

which leads to a value of 1.05 for the ratio

$$\frac{C^{14}_{\text{inorganic C}}}{C^{14}_{\text{biological C}}}$$

(Libby, 1955; Craig, 1954a). However, it turns out that application of the equilibrium ratio 1.05 is not justified, because the C^{14} content of modern marine shells is governed by a steady state rather than an equilibrium situation. This conclusion has emerged from a series of papers, which are discussed next.

Anderson and Libby (1951) and Kulp et al. (1951) reported that modern marine shells contained more C^{14} than modern wood. And indeed, Craig's (1953) finding of higher C^{13} contents in marine carbonates than in organic carbon from marine plants and animals suggested that an even greater enrichment of C^{14}, some 5 percent, should occur in the carbonates. However, additional measurements of marine shells by Suess (1954a, 1954b, 1955), deVries and Barendsen (1954), and Blau et al. (1953) all gave C^{14} contents essentially the same as that of modern wood. After showing that the low C^{14} activity of the shells cannot result from metabolic activity favoring deposition of C^{12}, Craig (1954a) concluded that modern bicarbonate in the surface waters of the ocean must have a radiocarbon age corresponding to the C^{14} deficiency (see also Suess, 1955; Rafter, 1955). Craig (1957a) later showed this situation resulted to a small extent from the slow transfer of carbon across the atmosphere-ocean interface, but principally from a piling-up of radiocarbon in the atmosphere and the mixed layer of the sea because of the slow internal mixing of the sea.

In special geographical areas, coastal upwelling of C^{14}-poor deep waters probably contributes to the deficiency of C^{14} in marine shells that grow there (Kulp et al., 1952). Crane (1956) and Brannon et al. (1957) noted that many modern shells in estuaries and restricted bays have abnormally low C^{14} concentrations. Johnson et al. (1957) suggested that this effect is analogous to the "hard-water-lake" effect discussed by Deevey et al. (1954), but they reported good consistency for samples from open-bay areas.

Post-depositional chemical changes involving replacement of some of the carbon atoms will, of course, alter the observed C^{14} content. Armstrong and Schubert (1947) could detect no C^{14} loss from C^{14}-enriched $BaCO_3$ during a 40-hour experiment in which H_2O vapor was absent. Unconsolidated soil carbonate from Bermuda showed no C^{14} enrichment, indicating that when only solution and transport, and no redeposition, are involved, there is no C^{14} exchange (Kulp et al., 1952; Craig, 1954a). Furthermore, five surface calcareous loess and soil samples examined by Münnich and Vogel (1959) had C^{14} contents of only 5 to 8 percent of the modern value. Broecker and Orr (1958) calculated the expectable effect for carbonates of varying porosity exposed to the atmosphere, but not to water, and claimed satisfactory agreement with experimental values obtained by analyzing CO_2 from layers of natural sample successively farther in from the surface. The finding of δO^{18} contents in pelagic foraminifera from Pacific cores that correspond to surface temperatures similar to those observed today has been taken to indicate that oxygen isotopic exchange with the much colder bottom water has not taken place and that the C^{14} contents are likewise reliable (Arrhenius et al., 1951). Similar reasoning has been applied to benthonic foraminifera of probable Oligocene age that give a paleotemperature higher than that of the present-day bottom waters (Emiliani and Edwards, 1953).

Bartlett (1951), Godwin (1951), and Deevey et al. (1954) pointed out that dead carbon dissolved from old limestone by water containing CO_2 in isotopic exchange equilibrium with the atmosphere may dilute the C^{14} content of this CO_2 by up to 50 percent. If $CaCO_3$ is precipitated from such waters before sufficient time has elapsed for reestablishment of isotopic exchange equilibrium with atmospheric CO_2, it will have an abnormally low C^{14} content. This phenomenon is expectable in freshwater lakes, which have much smaller carbon reservoirs than those of the surface ocean and the atmosphere and whose carbon isotopic composition is thus strongly dependent on that of entering river and spring water and on the ratio of the flushing rate of the lake to the rate of exchange with atmospheric CO_2 (Broecker and Orr, 1958). Caliche also presents a particularly complex problem because of the multiple solution and redeposition that has occurred at many localities.

Deevey et al. (1954) have studied samples from Queechy Lake, New York, which lies on metamorphosed Paleozoic limestone and is fed by waters that seep through old limestone and limestone-rich glacial drift. The carbonate and bicarbonate carbon in Queechy Lake water has a C^{14} activity appropriate for a solution, formed by atmospheric CO_2 acting on old limestone, that has proceeded about halfway to equilibrium (table 3). Some collodial $CaCO_3$ may have been included in this sample, obtained by acidification of water, but the C^{14} activities of both inorganic and organic materials produced in the lake are low.

Samples from Lake Zoar, Connecticut, which lies some 15 miles outside the region of limestone outcrop, are still deficient in C^{14}, although less so than those from Queechy Lake. Isotopic exchange equilibrium is apparently not fully achieved in 15 miles by the relatively shallow river which flows from the area of limestone outcrop into Lake Zoar. Blau et al. (1953) described marl from Pyramid Valley, North Canterbury, New Zealand, apparently deposited in a shallow, hard-water lake, which gives an excessive C^{14} age relative to that of peat which underlies it.

Deevey et al. (1954) suggested that in alkaline lakes in closed basins in semiarid regions not underlain by limestones, all of the carbon of the carbonate and bicarbonate in solution should be of atmospheric origin. Even if the streams were to dissolve some limestone containing only dead carbon, the presence of subsequent turbulent, high-gradient stretches in the streams could result in equilibration with atmospheric CO_2. Broecker and Orr (1958), however, found a C^{14}/C^{12} ratio for tufa currently forming in Pyramid Lake, Nevada, that was 5 percent lower than that of wood grown on the shores of the lake after normalization for C^{13}/C^{12} difference. The decrease in the C^{14}/C^{12} ratio of subaqueous plants in the lower portion of the Truckee River (which feeds Pyramid Lake), compared with that of the upper portion, indicated to Broecker and Walton (1959) that appreciable solution of carbonate from lacustrine sediments was taking place there. In their discussion of the geochemistry of C^{14} in freshwater systems, Broecker and Walton also used their measurements of Great Basin samples to evaluate the dependence of C^{14} concentration of dissolved bicarbonate upon rate of CO_2 exchange across the water-air interface and upon the relative amounts of silicate and carbonate minerals dissolved by the system.

Two factors have altered the C^{14} activity of the atmosphere during historical time. Combustion of coal has diluted the activity by an amount whose mean worldwide value is probably about 1 percent, although dilutions of as much as $3\frac{1}{2}$ percent may occur in industrial areas (Suess, 1955; Brannon et al., 1957). This so-called Suess effect typically has been determined by analyses of woods, but Brannon et al. claim the effect, to the extent of 1 or 2 percent, is detected in comparisons of open coastal water marine shells collected in 1850 and those collected today. Even more recently, the atmospheric C^{14} activity has been increased by atom bomb explosions (Rafter and Fergusson, 1957; deVries, 1958). There has hardly been time for this effect to be detected in shells grown in larger bodies of water, which must first equilibrate with the atmosphere.

STABLE CARBON ISOTOPES

The ratio of the two stable carbon isotopes, C^{12} and C^{13}, varies by about 5 percent in natural materials. Most carbonates are enriched in C^{13} relative to organic carbon, but some less common types of carbonates extend throughout the range. Craig (1957b) adopts for $10^5(C^{13}/C^{12})$ a value of 1123.00 for the sample of Solenhofen Limestone on which Nier (1950) earlier measured precise isotopic abundance ratios. The National Bureau of Standards Solenhofen Limestone standard (No. 20) has a very closely similar ratio, 1122.53.

During the depositional process, limestone becomes enriched in C^{13} some 0.3 percent, relative to the weighted mean for the active exchange reservoir of terrestrial plants + marine plants + ocean bicarbonate + atmospheric CO_2 (Craig and Boato, 1955). The four components of the reservoir have, respectively, 2.5, 1.3, 0.2, and 0.7 percent less C^{13} than average limestone. This slight increase of C^{13} in limestone during deposition contrasts with a 0.9 percent depletion of C^{13} for the over-all deposition of all sedimentary rocks, if a steady-state situation is assumed.

Carbon isotopic fractionation factors have been calculated for two reactions of particular interest in aqueous carbonate systems and have been experimentally measured for one of them. For the reaction

$$C^{13}O_2\ (g) + C^{12}O_3^{=}\ (aq) \rightleftharpoons C^{12}O_2\ (g) + C^{13}O_3^{=}\ (aq)$$

Urey and Greiff (1935) used estimated vibrational frequencies and calculated fractionation factors of 1.015 at 273.1° K, 1.012 at 298.1° K. They pointed out that constants such as the two given here, calculated from a theory for gases but applied to equilibrium between a gas and an ion dissolved in water, must necessarily be unreliable. Urey (1947) made a second calculation based upon then available natural abundances as well as upon spectroscopic data, and obtained 1.016 and 1.012. Craig (1953) suggested, on the basis of more reliable isotopic ratios for marine limestone and air, that the fractionation indicated by Urey's values should be approximately halved, that is, they should be changed to 1.008 and 1.006.

McCrea's (1950) calculated values for the fractionation factor for the reaction

$$C^{13}O_3^{=}\ (aq) + C^{12}O_3^{=}\ (s) \rightleftharpoons C^{12}O_3^{=}\ (aq) + C^{13}O_3^{=}\ (s)$$

between carbonate ions in the calcite structure and in aqueous solution are in agreement with the experimental values obtained when $CaCO_3$ is precipitated slowly; the factor is 1.0042 at 0° C and 1.0038 at 25° C. $CaCO_3$ precipitated very rapidly has the same carbon isotopic composition as the solution from which it formed.

Baertschi (1957) quoted a value of $\alpha = 1.010$ at 26° C for the reaction

$$C^{13}O_2\ (g) + C^{12}O_3^{=}\ (s) \rightleftharpoons C^{12}O_2\ (g) + C^{13}O_3^{=}\ (s)$$

based on unpublished experimental measurements. This number is the same as that obtained by multiplying together the fractionation factors for the two subreactions above, McCrea's 1.0038 and the 1.006 suggested by Craig.

The fractionation factors for these reactions are seen to be temperature dependent, but a temperature effect has not been detected in natural sedimentary materials, where it is presumably masked by other larger effects discussed below.

Although Jeffery et al. (1955) interpret some of their results in terms of changing isotopic composition of the carbon reservoir as a function of periodic diastrophism, most other workers are not convinced of the existence of this age effect (see also Compston, 1960).

The aqueous carbon reservoir, present chiefly as dissolved bicarbonate, is about 3×10^4 times smaller than the aqueous oxygen reservoir present as water (Baertschi, 1957), and thus the opportunity for local variations in reservoir composition are much greater for carbon. Jeffery et al. (1955) discussed the probable interrelationships among the carbon isotopic compositions of the several C-containing phases in closed aqueous systems, where the carbon reservoir no longer can be considered infinite relative to the amount of solid carbonate. Experimental data are generally not yet available for comparison with these theoretical predictions.

Variations in the C^{13}/C^{12} ratios of limestones were said by Craig (1953) to result from (1) variations in isotopic composition among the skeletal carbonates laid down by various organisms in the same environment; (2) local change in the composition of the aqueous carbon reservoir in the neighborhood of marine plants extracting CO_2 for photosynthesis; (3) possible equilibration of carbonate with organically derived CO_2; and (4) rate of carbonate precipitation. Values from a number of laboratories, assembled in table 4, may now be examined in terms of these effects. The values based on the Chicago CO_2 standard have always been reported in units of δC^{13}‰, where

$$\delta C^{13}‰ = \frac{C^{13}/C^{12}_{\text{sample}} - C^{13}/C^{12}_{\text{standard}}}{C^{13}/C^{12}_{\text{standard}}} \times 1000$$

Values from other laboratories have here been converted to δC^{13} (Chicago standard) wherever possible, using the relationships published by Craig (1957b). Some earlier results not included in this review have been discussed by Ingerson (1953).

Landergren (1954) published numerous carbon isotopic analyses demonstrating the occurrence of higher C^{12}/C^{13} ratios in Swedish limestones formed in environments where the contribution of large amounts of C^{12}-rich CO_2 from decomposing organic matter would be expectable. The gray Limbata Limestone, not so highly oxidized as the red variety, is found in areas corresponding to the deeper parts of the depositional basin and has a markedly higher B/Al ratio, indicating higher salinity and thus greater distance from nearshore freshwater influxes. The critical factor is the ratio in the immediate depositional environment between CO_2 of organic origin and that from the surface layer of the sea (shells, dissolved CO_2) in equilibrium with the atmosphere. A higher percentage of the available organic matter was oxidized in the depositional environment of the red Limbata facies, but equilibration with the atmosphere was apparently maintained. Landergren's bituminous limestones are also somewhat enriched in C^{12}, relative to typical open marine limestones, but it is the small amounts of carbonate contained in red clays and shales that show the greatest C^{12} enrichments.

Silverman and Epstein (1958) reported several δC^{13} values for organic material contained in carbonate sediments. The material extractable with a 4:1 chloroform:methanol mixture from a core taken in the shallow water of Florida Bay, Florida Keys, gave values from -20.3 to -26.2‰ at depths in the 60-inch to 80-inch range. The total organic matter in the surface mud off Lignum Vitae Island in the Florida Keys averages -13.5‰. In distinguishing between marine and nonmarine environments, it appears to be significant that the δC^{13} values of petroleums and organic extracts from marine sediments range from -22.2 to -29.4‰, whereas those for comparable organic materials derived from nonmarine sediments range from -29.9 to -32.5‰.

Mere contiguity of organic matter and carbonate does not of course indicate that isotopic exchange has occurred. Wickman (1953) found that the C^{12}/C^{13} ratios of most of the carbonates present as small amounts in coal that he examined did not indicate that significant amounts of CO_2 of organic origin had participated in their formation.

Although agreeing with Landergren's interpretation of the Swedish carbonates, Jeffery et al. (1955) noted a poor correlation in Australian limestones between isotopic composition and oxidation state as revealed by color and suggested that other factors may be involved. However, their samples were from widely scattered sources, geologically and geographically, and they did not compare, as Landergren did, large numbers of samples from different facies of the same horizon.

The general lowering of δC^{13} values of cold-water carbonates (from caves, soil concretions, and other such sources) below values expectable for carbonates formed from normal atmospheric CO_2 was attributed by Baertschi (1957) to the incorporation of CO_2 derived from oxidation of organic matter in the water and in soil humus zones. The secondary carbonate veinlets examined by Baertschi always contained less C^{13} than did the host rocks. Vogel (1959) stated that in freshwater carbonate deposition C^{13}-poor CO_2 formed in the soil humus zone by humus decomposition and by plant-root respiration is important. Craig (1953) likewise concluded that his extremely light travertine, tufa, and stalactite carbonate values probably resulted from equilibration of carbonate with organically-derived CO_2 (see also the results of Münnich and Vogel, 1959). The high δC^{13} values for Baertschi's Engadine tufas and that for cold-water travertine precipitated from the Tivoli River (Craig, 1953) are striking exceptions to the generalization suggested by these several authors. Vogel (1959) suggested that isotopic equilibration between magmatic CO_2 (derived from thermal decomposition of limestone) and bicarbonate in solution could yield a solution capable of precipitating these C^{13}-rich travertines.

The samples of calcite from salt-dome caprocks described by Thode et al. (1954) and by Feely and Kulp (1957), the lightest carbonates recorded thus far, have δC^{13} values as low as -51‰. The isotopic compositions found for C and S are reasonable for a process involving bacterial reduction of sulfate to form H_2S and S, and oxidation of organic matter to CO_2 and H_2O (see also Ault, 1959). Formation of the calcite and sulfur by a localized process involving organisms also is suggested by the isotopic variations of C and S in the same core sample.

The relatively heavy $CaCO_3$ found by Craig (1953) in chalks, and the even greater C^{13} content of $CaCO_3$ from modern marine plants (algae) led him to postulate that algal withdrawal of C^{12}-rich CO_2 for photosynthesis had changed the pH of the surrounding water and led to precipitation of the C^{13}-rich $CaCO_3$ making up the chalks. Urey et al. (1951) had noted earlier that δC^{13} values for belemnites of Upper Cretaceous age showing apparently unaltered δO^{18} values were erratic, and ascribed the variation to fractionation of C isotopes by plants and a consequent large effect on the relatively small carbon reservoir in the ocean. Although some of the chalk matrices examined by Urey et al. are lighter than the contained fossils, both chalks and fossils are significantly heavier than modern invertebrate skeletal material (see table 4).

The carbonates in the lacustrine Green River Formation have a high δC^{13} value of about 2‰, in sharp contrast to the -31.9‰ for the associated organic matter (Silverman and Epstein, 1958). Not only has post-depositional exchange between carbonate and organic material obviously not occurred to any significant extent, but the extreme spread in the two values appeared to Silverman and Epstein to require explanation. They suggested that concurrent algal photosynthesis and carbonate precipitation took place in a thermally stratified lake whose warm surface-water layer was relatively poor in bicarbonate because of the algal activity. Support for this model is given by Wickman's (1952) finding that lacustrine plants living in stagnant water have δC^{13} values averaging 8.8‰ less than those from nonstagnant water. Craig (1954a) obtained a C^{13} range of 9‰ for freshwater plants grown in stagnant tanks, correlatable with the amount of carbonate precipitated, and suggested that rate and source of supply of CO_2 are critical.

The δC^{13} values for freshwater limestones (Clayton and Degens, 1959) are consistently lower than those for marine limestones (table 4). The same relation was noted for seven carbonate fractions present to the extent of 2 to 5 percent in marine and nonmarine sandstones, but no such regular relationship was found in the C isotopic composition of a number of carbonates examined that make up less than 0.5 percent of somewhat bituminous shales of Pennsylvanian age. The contribution from detrital carbonate fragments may become important in the latter case, and the concentration of both living organisms and decaying organic matter in the depositional environment makes possible either enrichment or depletion of C^{13} in the carbonate, depending upon the immediate local situation.

The preservation of most of the δC^{13} differences between nonmarine and marine carbonates, even for Paleozoic rocks, is in contrast to the behavior of oxygen isotopes in the same samples. Wickman and von Ubisch's early (1951) finding that two generations of calcite crystals in a vug in reef limestone of Silurian age were successively poorer in C^{13} than the limestone suggests incomplete equilibration of the rock with nonmarine waters in contact with organic matter.

Craig (1953) suggested that the high C^{13} content of oolite of Cambrian age from Tyrone, Pennsylvania, resulted from rapid precipitation in shallow, strongly agitated water. However, this explanation seems a dubious one in view of laboratory experiments by Lowenstam and Epstein (1957) that show it is difficult to precipitate $CaCO_3$ from supersaturated but dilute solutions at the pH of ocean water rapidly enough to prevent isotopic equilibrium from being attained.

The carbon isotopic compositions of several dolomites analyzed by Wickman et al. (1951) fell in the heavier part of the range for limestones. Craig (1953) gave a few more analyses and concluded that not enough data were available to justify concluding that the relationship observed by Wickman holds generally.

MAGNESIUM ISOTOPES

Daughtry et al. (in press) measured Mg^{24}/Mg^{26} values in traverses across tectonically localized dolomite bodies and found the ratios progressively lower for samples successively farther from faults.

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TABLE 1 - OXYGEN ISOTOPIC COMPOSITION OF CARBONATE SEDIMENTS, SKELETAL MATERIALS, AND ROCKS

In units of δO^{18} relative to the Chicago PDB standard (Craig, 1957b)

Only the values of Clayton and Degens (1959) have been corrected for difference of C^{13} content of sample and standard, the second term in Craig's equation

$$\delta_c O^{18} = 1.0014\,\delta_m + 0.009\,\delta C^{13}$$

For the range of C^{13} contents of natural carbonates, neglect of this correction would cause a false spread in δO^{18} of 0.6°/oo. Baertschi's (1957) values, for which he assumed $\delta_c = \delta_m$, represent a further degree of approximation, although for small values of δO^{18} neither of the two corrections is important.

The analytical fractionation introduced during treatment of the Ca-Mg carbonate samples with 100% H_3PO_4 at 25°C, which liberates only two-thirds of the oxygen in the carbonate, was assumed by Clayton and Epstein (1958) and Engel et al. (1958) to be the same as the 1.010 value determined by Clayton and Epstein for $MnCO_3$, from which all the oxygen can be extracted by a carbon reduction method. Clayton (1959) now reports 1.0075 for $CaCO_3$, based upon an extrapolation of experimental data to K = 1, and use of this value would reduce quartz-calcite fractionations reported below by 2.5°/oo. If the analytical fractionation differs for different carbonates, the further possibility exists that the dolomite data should be shifted by an unknown amount.

Material	δO^{18} in °/oo	
Pleistocene pelagic foraminifera, Atlantic and Pacific Oceans (Emiliani, 1955a)	Range	-2.10 to +1.92
Pleistocene benthonic foraminifera (Emiliani, 1955a)		
Atlantic Ocean, glacial periods	Av.	+4.07
Atlantic Ocean, interglacial periods	Av.	+2.84
Pacific Ocean, glacial periods	Av.	+3.68
Pacific Ocean, interglacial periods	Av.	+3.45
Bahama Bank materials (Lowenstam and Epstein, 1957)*		
23 algal aragonites	Range	-3.1 to +1.5
	Av.	-1.0
9 samples, sedimentary aragonite needles	Range	-0.5 to +0.5
	Av.	+0.1
12 samples, oolites and grapestones	Range	-0.4 to 0.0
	Av.	-0.1
3 serpulid worm tubes, *Salmacina* sp.		-0.4, -0.4, +0.7
Venus sp., modern, marine (Clayton and Degens, 1959)		-1.37
71 modern mollusks, Bermuda (Epstein and Lowenstam, 1953)	Range	-1.8_8 to $+0.4_7$
33 mollusks from interglacial Pleistocene deposits, Bermuda (Epstein and Lowenstam, 1953)	Range	-1.1_2 to -0.0_4
Unio sp., modern, nonmarine (Clayton and Degens, 1959)		-7.42
Helix sp., modern, nonmarine (Clayton and Degens, 1959)		-8.46
Modern Hawaiian lake mud, nonmarine (Clayton and Degens, 1959)		-8.39
Pleistocene age varved clay, New York (Clayton and Degens, 1959)		-8.05
Four calcareous tufas, Engadine springs	Range	-10.6 to -9.4
(Baertschi, 1957)**	Av.	-10.2
White carbonate precipitate, Pfäfer spring (Baertschi, 1957)**		-21.4
Calcareous concretion in loam (Baertschi, 1957)**		-6.3
Calcareous onyx, Pueblo, Mexico (Baertschi, 1957)**		0.0

TABLE 1 - continued

Material	δO^{18} in ^{o}/oo	
6 other freshwater deposits (Baertschi, 1957)**	Range	-4.7 to -20.2
	Av.	-9.1
40 specimens *Belemnitella americana*, Upper Cretaceous, southeastern U. S. (Urey et al., 1951)	Range	-0.4_3 to -0.0_9
Upper Cretaceous of England (Urey et al., 1951)		
8 brachiopods	Range	-2.8_3 to -1.4_6
11 oysters	Range	-3.6_8 to -1.8_5
6 belemnites	Range	-2.0_3 to -0.4_0
11 chalk matrices	Range	-3.8_5 to -1.8
Three Danish belemnites (Urey et al., 1951)	Range	-0.4_3 to -0.0_9
Albian and Upper Cretaceous age samples, mostly from western Europe, southeastern United States (Lowenstam and Epstein, 1954)		
191 belemnites	Range	-2.9_7 to $+0.8_8$
10 brachiopods	Range	-2.8_3 to -0.0_2
19 *Inoceramus* fragments	Range	-3.5_6 to $+0.1_1$
51 Ostreidae	Range	-3.8_0 to -0.6_4
63 associated chalks	Range	-3.7_4 to -0.3_3
	Av.	-2.0_3
11 Paleozoic marine limestones (Clayton and Degens, 1959)	Range	-12.48 to -5.11
	Av.	-8.48
Two nonmarine Miocene age limestones, and an included fossil, Idaho (Clayton and Degens, 1959)	Range	-18.49 to -16.79
	Av.	-17.88
Two nonmarine Tertiary age limestones, Kansas (Clayton and Degens, 1959)	Range	-7.39 to -6.67
	Av.	-7.03
10 nonmarine Pennsylvanian age limestones, Pennsylvania (Clayton and Degens, 1959)	Range	-9.00 to -5.04
	Av.	-7.26
4 marine limestones, comparison of matrix with calcite veins (Baertschi, 1957)**		-4.6, -6.4
		-3.0, -9.6
		-5.2, -6.6
		-3.3, -4.2
Belemnite, Gallovien age (Baertschi, 1957)**		0.0
Crinoids from Carboniferous-Devonian age limestone (Baertschi, 1957)**		-2.3
Olenus truncatus, Upper Cambrian (Baertschi, 1957)**		-7.4
4 Devonian age brachiopods from Australia that probably have undergone post-depositional isotopic re-equilibration (Compston, 1960)†	Range	-5.5 to -3.6
24 Permian age brachiopods from Australia, believed to be isotopically preserved (Compston, 1960)†	Range	-3.7 to +2.2
	Av.	-0.5
Calceolispongia, basal plate, Permian of Australia (Compston, 1960)†		-6.8
Precambrian age dolomite (Baertschi, 1957)**		-6.8
Precambrian age algal limestone (Baertschi, 1957)**		-5.4
15 other limestones, Tertiary to Ordovician age (Baertschi, 1957)**	Range	-6.1 to -2.8
	Av.	-4.2
6 samples of Leadville Limestone, Mississippian age, Colorado, 2 dolomitic (Engel et al., 1958)‡	Range	-8.3 to -0.9
	Av.	-4.9
δO^{18} determinations for quartz-calcite pairs, given in that order (Clayton and Epstein, 1958)‡		
Black chert in chalk; Cretaceous; France		+4.5, -2.7
Black chert in Mississippian limestone, Fulford, Colorado		-0.3, -6.7

TABLE 1 - continued

Material	δO^{18} in $^o/oo$
Small calcite crystals embedded in "Herkimer diamonds" (quartz crystals in cavities in dolomite), Herkimer County, N.Y.	-5.5, -10.7
Black chert in recrystallized Mississippian limestone; Fulford, Colorado	-7.2, -11.6
Chert and dolomite in Leadville Formation, Meeker, Colorado	-1.8, -0.9
Quartz and recrystallized dolomite, Marble, Colorado	-6.4, -6.4

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* Salinity variations in the various waters from which these samples were collected resulted in the waters' having δO^{18} values from about +1.6 to +3.2 relative to mean ocean water. If the carbonate δO^{18} values are corrected to what they would have been if deposition had taken place from water having $\delta O^{18} = 0$, the average δO^{18} for algal aragonite becomes -3.1, for aragonite needles, -2.7, for oolites, -1.8.

† Not including determinations that Compston indicated may be irregularly up to 2.0 $^o/oo$ too positive because of variation in the temperature at which carbonate decomposition was carried out.

** Reported as δO^{18} relative to the Basel standard, and here converted to δO^{18} relative to the Chicago standard, using the relation given by Craig (1957b).

‡ Reported as δO^{18} relative to Hawaiian ocean water and to mean ocean water, whose difference of 0.2 $^o/oo$ was ignored, and here computed as δO^{18} relative to the Chicago PDB standard using the relation given by Clayton and Epstein (1958):

$$\delta_{OW} = 1.0295\,\delta_{PDB} + 29.5$$

TABLE 2 - C^{14} ACTIVITY OF CONTEMPORARY SHELLS

In absolute disintegrations per minute per gram (after Libby, 1955)

All analyses quoted from other laboratories have been reduced by Libby by assuming that the modern wood assay is in perfect agreement with his average value for terrestrial biosphere samples, 15.3 ± 0.1 Dpm/g. The values given by Kulp et al. (1951) have since been reported to be too high (see Craig, 1954a).

Four seashells from Lower California (Suess, 1954b)	15.3 ± 0.2
Six clam shells, New York (Kulp et al., 1951)	16.9 ± 0.3
Bikini coral (*Halimeda* debris) (Kulp et al., 1951)	16.9 ± 0.3
Clam shells, Aleutians (Kulp, Tryon et al., 1952)	13.3 ± 0.5
Eleven mollusk shells, North America (Blau et al., 1953)	15.8 ± 0.2
Same, excluding two high values at 17.8 and 17.2	15.4 ± 0.2
Murex shell, Florida	17.1 ± 0.5
Fresh ocean sediment, Bermuda	17.4 ± 0.5
Oyster, Chesapeake Bay	15.1 ± 0.5

TABLE 3 - C^{14} ACTIVITY OF MATERIALS FROM QUEECHY LAKE, NEW YORK
(After Deevey et al., 1954)
In counts per minute

Average of modern woods, Connecticut	5.86 ± 0.08	Average 6.02
Submerged vegetation, Conn. soft-water lakes	6.15 ± 0.08	
CO_2 from $CO_3^=$ and HCO_3^-, Queechy Lake water	4.60 ± 0.10	
Chara sp. , inorganic calcareous material	5.02 ± 0.10	
Organic carbon	5.07 ± 0.10	
Potamogeton sp., inorganic calcareous material	5.02 ± 0.11,	5.09 ± 0.11
Organic carbon	4.99 ± 0.11,	5.18 ± 0.16
Elliptio complanatus, shell	5.20 ± 0.14,	4.87 ± 0.07
Soft parts	4.83 ± 0.11,	4.82 ± 0.08
Deep-water muds	4.68 ± 0.09,	4.97 ± 0.15
Scirpus sp. (emergent)	6.00 ± 0.10	

TABLE 4 - STABLE CARBON ISOTOPIC COMPOSITION OF CARBONATE SEDIMENTS, SKELETAL MATERIAL, AND ROCKS
In units of δC^{13} relative to the Chicago PDB standard (Craig, 1957b)

Values in parentheses are expressed relative to other standards for which conversion factors are not available. Only the values of Baertschi (1957), Clayton and Degens (1959), and Compston (1960) have been corrected for differences in O^{17} abundances of sample and standard, in addition to the customary correction for the O^{17} content of the standard. For the range of oxygen isotopic compositions encountered in carbonates, the former effect corresponds to a spread of 1 $^o/_{oo}$ in C^{13}.

Material		δC^{13} in $^o/_{oo}$
Atmospheric CO_2 (Craig, 1953)		-7.4 to -9.9
Atlantic Ocean bicarbonate (Craig, 1954a)		-1.3 to -2.9
Modern pelagic foraminifera, equatorial Atlantic (Craig, 1954a)		+1.2
Modern pelagic foraminifera, equatorial Pacific (Craig, 1954a)		+1.9
Modern skeletal carbonates (Craig, 1953)		
Echinoderm, *Arbacia*		-3.5
Echinoderm (starfish)		-5.9
Gastropod, *Leucozonia cingulifera*		-0.3
Coral, *Porites porites*		-1.4
Gastropod, *Fasciolaria tulipa*		+0.4
Five modern marine algal carbonates (Craig, 1953)	Range	-4.5 to +4.3
	Av.	+2.0
Same, excluding value of -4.5	Range	+3.1 to +4.3
	Av.	+3.6
Bahama Bank materials (Lowenstam and Epstein, 1957)		
23 algal aragonites	Range	+0.1 to +5.9
	Av.	+3.8
9 samples, sedimentary aragonite needles	Range	+2.8 to +4.9
	Av.	+3.6
12 samples, oolites and grapestones	Range	+3.2 to +5.2
	Av.	+4.7
3 serpulid worm tubes, *Salmacina* sp.		+2.6, +3.7, +4.2
12 modern marine mollusks (Craig, 1954a)	Range	-3.8 to +1.9
	Av.	-0.1

TABLE 4 - continued

		δC^{13} in $^{o}/oo$
10 carbonate samples from basin sediments off southern California (T. A. Rafter, *in* Emery, 1960)	Range Av.	-1.9 to +0.9 -0.1
7 samples, carbonate from Romanche Deep core, Atlantic Ocean, S 00° 07', W 18° 12' (Landergren, 1954)*	Range Av.	-2.4 to -1.0 -1.8
4 samples, small amounts of carbonate in red clays, Pacific (Landergren, 1954)*	Range Av.	-13.1 to -6.1 -10.1
13 freshwater deposits (concretion, fissure filling, cave and spring deposits) (Münnich and Vogel, 1959)	Range Av.	(-10.2 to -4.6)* (-8.2)*
5 surface samples of calcareous soil and loess (Münnich and Vogel, 1959)	Range Av.	(-1.6 to +1.6)* (-0.3)*
Caliche, Kansas (Craig, 1954a)		-0.3, -0.6
Travertine, Tivoli River, near Rome (Craig, 1953)		+9.8
"Hot water ice" ($CaCO_3$ crust on surface of still pools), Angel Terrace, Yellowstone National Park (Craig, 1953)		+3.6
"Globular shells" ($CaCO_3$ formed around gas bubbles), Angel Terrace, Yellowstone National Park (Craig, 1953)		+3.4
Post-Cretaceous age travertine, Suisun, California (Craig, 1953)		-6.7
Stalactite, Blue Mounds Cave, Wisconsin (Craig, 1953)		-8.9
Travertine, Great Salt Lake (Craig, 1953)		-10.1
Travertine, Silver Gate, Yellowstone National Park (Craig, 1953)		+5.9
Four calcareous tufas, Engadine springs (Baertschi, 1957)†	Range Av.	+6.3 to +11.0 +9.1
White carbonate precipitate, Pfäfer spring (Baertschi, 1957)†		-15.8
Calcareous concretions in loam (Baertschi, 1957)†		-8.5
Calcareous onyx, Pueblo, Mexico (Baertschi, 1957)†		+3.2
6 other freshwater deposits (Baertschi, 1957)†	Range Av.	-9.4 to -2.1 -6.0
7 loess samples (Vogel, 1959)**	Range Av.	-4.4 to -0.6 -2.5
Lösskindel (Vogel, 1959)**		-8.1
7 calcareous sinters and stalagmites (Vogel, 1959)**	Range Av.	-9.2 to -6.5 -8.2_5
5 water samples, Heidelberg region (Vogel, 1959)**	Range Av.	-14.3 to -12.9 -13.3
5 water samples, brown coal region near Cologne (Vogel, 1959)**	Range Av.	-17.6 to -14.1 -15.6
Fossils and matrices from Upper Cretaceous of England (Urey et al., 1951)		
8 brachiopods	Range	$+1.3_9$ to $+2.9_0$
11 oysters	Range	$+0.7_9$ to $+2.8_4$
6 belemnites	Range	$+0.4_6$ to $+3.2_0$
22 chalk matrices	Range	$+0.7_1$ to $+2.8_1$
9 Devonian age brachiopods from Australia, most of which have undergone post-depositional isotopic re-equilibration (Compston, 1960)	Range Av.	-0.2 to +1.9 +0.6
Recrystallized and infilled portions of Devonian age fossils from Australia (Compston, 1960)	Range	-4.1 to -0.3
31 Permian age brachiopods from Australia, believed to be isotopically preserved (Compston, 1960)	Range Av.	-2.7_4 to +5.8 +4.3
9 Permian age crinoids from Australia, believed to have undergone post-depositional isotopic re-equilibration (Compston, 1960)	Range	-17.0 to +4.7

TABLE 4 - continued

		δC^{13} in $^o/oo$
Belemnite, Gallovien age (Baertschi, 1957)†		+0.3
Crinoids from Carboniferous Devonian age limestone (Baertschi, 1957)†		+2.5
Olenus truncatus, Upper Cambrian (Baertschi, 1957)†		+0.7
Silurian age limestone, Gotland (Wickman and von Ubisch, 1951)*		
Matrix		+4.6
Older calcite crystals in vug		+2.5
Younger calcite crystals in vug		+1.2
26 salt-dome calcite caprock samples (Feely and Kulp, 1957)	Range	(-43.8 to -23.9)‡
	Av.	(-35.2)‡
6 calcites from salt-dome caprocks (Thode et al., 1954)#	Range	-51.1 to -30.9
	Av.	-41.8
Lacustrine Green River Formation (Silverman and Epstein, 1958)		+2.0
Limestones and fossils, mostly Australian (Jeffery et al., 1955)		
9 Tertiary	Range	-8.1 to +1.7
	Av.	-5.6
4 Mesozoic	Range	-1.2 to +2.0
	Av.	+0.1
6 Upper Paleozoic	Range	-12.7 to +2.1
	Av.	-1.6
8 Devonian	Range	-1.7 to +4.7
	Av.	+1.2
14 Cambrian and Silurian	Range	-2.9 to +2.0
	Av.	-0.8
	Over-all Av.	-1.5
4 marine limestones, comparison of matrix with calcite veins (Baertschi, 1957)†		-0.8, -4.8 +1.8, +1.3 +1.5, -0.3 +0.8, +0.4
6 samples Leadville Limestone, Mississippian age, Colorado (Engel et al., 1958)	Range	-2.8 to +0.8
	Av.	-0.7
19 nonmarine shells, sediments, and limestones, modern-Pennsylvanian (Clayton and Degens, 1959)	Range	-17.69 to -2.59
	Av.	-6.66
4 modern and Pleistocene samples	Range	-17.69 to -5.54
	Av.	-10.06
5 Tertiary limestones and fossils	Range	-6.74 to -2.82
	Av.	-5.23
10 Pennsylvanian limestones	Range	-9.79 to -2.59
	Av.	-6.02
12 marine shells and limestones (1 modern, 1 Devonian, rest Pennsylvanian) (Clayton and Degens, 1959)	Range	-3.96 to -0.16
	Av.	-1.54
20 samples of calcite present in small amounts in coal (Wickman, 1953)*	Range	-19.2 to +8.3
	Av.	-2.9
15 samples, reddish variety of Lower Ordovician Limbata Limestone, Sweden (Landergren, 1954)*	Range	-1.0 to +1.8
	Av.	+0.3
18 samples, gray variety of Limbata Limestone (Landergren, 1954)*	Range	-6.7 to +0.4
	Av.	-1.8
7 samples, Lower Ordovician age Planimbata Limestone, Sweden (Landergren, 1954)*	Range	-2.2 to +1.0
	Av.	-0.6
7 samples, Cambrian and Ordovician age bituminous limestone, Sweden (Landergren, 1954)*	Range	-4.2 to -1.0
	Av.	-2.6

TABLE 4 - continued

		δC^{13} in $^{o}/_{oo}$
51 samples, Upper Ordovician age algal limestone, borehole, Gotland (Landergren, 1954)*	Range	-1.0 to +3.9
	Av.	+0.7
Small amounts of carbonate in shales (Landergren, 1954)*		
38 samples, alum shale	Range	-15.1 to -6.4
	Av.	-10.6
20 samples, *Dictyonema* shale	Range	-12.4 to -6.0
	Av.	-9.0
7 samples, various black shales	Range	-10.4 to +0.1
	Av.	-5.2
Precambrian age dolomite (Baertschi, 1957)†		+8.0
Precambrian age algal limestone (Baertschi, 1957)†		+3.9
15 other limestones, Tertiary to Ordovician in age (Baertschi, 1957)†	Range	-0.8 to +2.8
	Av.	+1.3
21 marine limestones, Cambrian to Pleistocene age (Craig, 1953)	Range	-3.3 to +2.4
	Av.	-0.2
Spergen Limestone (Microcoquina), Mississippian age, Indiana		+2.4
Chalk, Cretaceous age, Dover, England		+2.0
Chalk, Cretaceous age, Mississippi		+1.4
Chalk, Cretaceous age, Colorado		+1.0
Randville Dolomite, Dickinson Co., Michigan, with algal structures		+1.1, +1.2
Same without algal structures.		+1.1, +1.2

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* Stockholm results quoted in units of C^{12}/C^{13} have been converted to δC^{13} relative to the Chicago PDB standard, using the relation (Harmon Craig, personal communication)

$$\delta C^{13} = \left(\frac{88.585}{C^{12}/C^{13}} - 1\right) 1000$$

** Standard, "Solenhofen Limestone," is not defined further.

† Reported by Baertschi as δC^{13} relative to the Basel standard, and here recomputed to δC^{13} relative to the Chicago standard using the relations given by Craig (1957b).

‡ Primary standard is "sedimentary limestone."

Reported by Thode et al. as the ratio of $(C^{12}/C^{13})_{sample}$ to that of the Chicago standard, 88.89, and here recomputed as δC^{13} relative to 88.99 for the Chicago standard (see Craig, 1957b).

SELECTED CHEMICAL ANALYSES OF CARBONATE SEDIMENTS AND ROCKS

Percentages given in parentheses are analytically determined quantities that are not included in the total because of duplication, for example, CO_2 vs. loss on ignition

	ANALYSIS NUMBER					
	(1)	(2)	(3)	(4)	(5)	(6)
SiO_2	18.8	8.21	58.6	52.8	54.48	5.19
TiO_2	0.3	0.14	0.9	0.9	0.98	0.06
Al_2O_3	5.1	4.14	15.9	16.4	15.94	0.81
Fe_2O_3	3.8	4.09	11.8	9.0	8.66	0.54
FeO					0.84	
MnO	0.4	0.54	1.2	1.0		0.05
CaO	39.0	44.55	2.8	7.7	1.96	42.61
MgO	1.4	0.83	4.4	2.9	3.31	7.90
SrO					0.056	None
BaO					0.20	None
Na_2O	0.5	1.32	1.6	1.7	2.05	0.05
K_2O	0.7	0.78	2.2	2.7	2.85	0.33
Li_2O						Trace
P_2O_5	0.2	0.26	0.6	0.3	0.30	0.04
CO_2	29.8	34.75		4.6		41.58
H_2O (-)					7.04	0.21 (110°C)
H_2O (+)						0.56*
Cl		0.31				0.02
SO_3						0.05
ZrO_2		0.08				
S						0.09
MnO_2					1.21	
Total	100.0	100.0	100.0	100.0	100.000†	100.09

(1) Average composition of calcareous sands and oozes, on a water-free basis (Poldervaart, 1955, recalculated from unpublished averages of W. W. Rubey).

(2) Average composition of *Globigerina* oozes from 66 stations (Sujkowski, 1952), modified to include CO_2. All CO_2 is assumed to be combined with CaO, and the amount of noncarbonate CaO is fixed by assuming it has the same ratio to TiO_2 as in analysis (5).

(3) Analysis (1) recalculated to a $CaCO_3$-free basis for comparison with analyses of red clay. All CO_2 in (1) has been assumed to be combined with CaO.

(4) Average composition of red clay on a water-free basis (Poldervaart, 1955, recalculated from unpublished averages of W. W. Rubey).

(5) Composite analysis of 51 samples of red clay, computed on a $CaCO_3$-free basis. Analyst, George Steiger, U. S. Geol. Survey, with special determinations by W. F. Hillebrand and E. C. Sullivan (Clarke, 1924). † Total also includes 0.012% Cr_2O_3, 0.039% NiO + CoO, 0.035% V_2O_3, 0.001% As_2O_3, Trace MoO_3, 0.024% CuO, 0.008% PbO, 0.005% ZnO.

(6) Composite analysis, by H. N. Stokes, of 345 limestones (Clarke, 1924).
* Includes organic matter.

	ANALYSIS NUMBER							
	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
SiO_2	16.98	8.40	19.24	26.67	0.6	0.48	3.03	Sand 7.98 Sol. SiO_2 0.25
TiO_2					0.1	0.02	0.0065	
Al_2O_3	6.44	3.15	3.26	0.91	5.5	0.23	0.18	None
Fe_2O_3	1.40	3.75	1.09	0.64	3.0	0.29	0.31	0.21
MnO			Trace	Trace				
CaO	29.73	44.00	38.94	36.40	27.6	44.62	51.44	51.60
MgO	8.25	0.47	2.75	0.51	1.7	8.57	1.02	Trace
Na_2O	0.28		Trace	Trace			0.38	0.11
K_2O	0.14		Trace	Trace			0.12	Trace
P_2O_5			0.23	0.75	4.0	*	0.065	Trace
CO_2	32.52	33.20	29.57	25.84			40.83	40.11
H_2O (-) H_2O (+)	4.47		1.67	2.26			1.78	0.17
Cl			0.11	0.07			Trace	0.08
SO_3			0.53	0.82			0.55	Trace
Ign. loss		6.7			55.5			
Org. matter			2.96	5.10				
Insol. res.							None	
N							0.03	
As_2O_3							0.012	
Total	100.21	99.67	100.35	99.97	98.0		99.75	100.51

(7) Sediment from the Isar River, Germany, containing abundant material from glacial deposits; rich in carbonates, including dolomite (Sauer, 1938).

(8) Alluvium, banks of Shoal Creek near Austin, Travis County, Texas. J. E. Stullken, analyst (Schoch, 1918).

(9) Adobe soil, Salt Lake City, Utah. Analyst, L. G. Eakins, U. S. Geol. Survey (Clarke, 1924).

(10) Adobe soil, Fort Wingate, N. M. Analyst, L. G. Eakins, U. S. Geol. Survey (Clarke, 1924).

(11) Hikutavake rocky silt loam, Niue Island, South Pacific (Schofield, 1959), Dominion analyst.

(12) Average of four limestone analyses, Niue Island, South Pacific (Schofield, 1959), Dominion analyst. *One of the four analyses gave P_2O_5, 0.08.

(13) Oolite at Black Rock, Great Salt Lake. George Cronkheit, analyst. (Eardley, 1938).

(14) Oolite, Everglades, Florida. W. C. Wheeler, analyst (Clarke, 1915).

ANALYSIS NUMBER

	(15)	(16)	(17)		(18)	(19)
			Range	Average		
SiO_2	1.88	0.53	0.43-16.88	9.07	19.42	6.56
TiO_2			0.00- 0.13	0.05		
Al_2O_3	0.36	0.14	0.06- 2.15	0.85	1.21	1.71
Fe_2O_3	0.27	0.96*	0.24- 2.43	0.93	0.25	0.63
MnO		Trace	0.10- 0.28	0.18		
CaO	52.89	51.87	30.82-51.61	42.75	28.61	23.94
MgO	0.76	1.10	1.11- 1.81	1.46	9.42	15.07
Na_2O		0.10	0.03- 0.30	0.14		3.73
K_2O		0.10	0.00- 0.39	0.16		0.28
P_2O_5		0.06	0.02- 0.15	0.09		
NaCl					4.29	
CO_2		42.30	25.00-41.66	34.62	32.50	33.76
H_2O (-)		0.97	0.54- 2.78	1.39	1.84	9.40
H_2O (+)		1.22				
SO_3		0.14	0.40- 1.13	0.69	0.43	2.16
Org. matter					0.17‡	
Ign. loss	43.73		3.41-16.18†	7.57		
Cl						4.09
S						0.20
Total	99.89	99.49	99.79-100.40	99.95	98.14	100.61

(15) Pisolite deposited from hot springs, San Antonio, Texas. W. C. Wheeler, analyst (Wells, 1937).

(16) Marl, Ore Lake, Michigan. E. C. Sullivan, analyst (Clarke, 1915). *Total Fe as Fe_2O_3.

(17) Ranges and average values for 9 analyses of marls from Minnesota lakes (Goldich et al., 1959). † Total loss on ignition, minus CO_2 and H_2O (-).

(18) Dolomite-bearing lake sediment, South Australia, (Alderman and Skinner, 1957). Contains precipitated celesite (H. C. W. Skinner, personal communication). ‡Acid-insoluble organic matter as carbon.

(19) Dolomite-bearing sediment, 12 feet below surface, Lake Eyre (Bonython, 1956; T. R. Frost, analyst). Quartz, kaolinite, dolomite, illite, palygorskite, and gypsum are identified in X-ray powder diagrams taken by Dr. K. Norrish and Mrs. L. Rogers.

	ANALYSIS NUMBER					
	(20)	(21)	(22)	(23)	(24)	(25)
SiO_2	14.41		7.52†		0.25	1.81
TiO_2	0.24					Trace
Al_2O_3	2.77	1.26*	1.77	1.06	0.56	0.32
Fe_2O_3	1.31					0.04
FeO	1.40					
MnO	0.02	28.4				0.01
CaO	26.95	1.26	1.18	1.84	51.52	52.18
MgO	11.61	23.64	38.28	36.40	2.08	0.86
Na_2O	0.82					0.61
K_2O	0.77					0.10
P_2O_5	0.13					0.07
CO_2	31.52	18.21	34.97	23.71	41.58	42.04
H_2O (-)	1.72	13.65	1.06(105°C)	20.81	3.19	0.22(105°C)
H_2O (+)	3.46		15.41			
Cl	0.14					
SO_3	0.51					
S	0.11					
Insol. res.				14.93		(2.53)
Vol. matter						(1.43)
Ign. loss						(43.37)
FeS_2						0.32
Org. C	1.84	8.40				
"Elements of organic matter"	1.33					
Total	101.06	94.82	100.19	98.75	99.18	98.58

(20) Uniformly fine-grained bottom sediment, Biurlju-Tiupinskij pool of Lake Balkhash (Zalmanson, 1951).

(21) Sediment in Lake El'ton (Vital, 1951). * R_2O_3.

(22) Hydromagnesite (?) deposit, Bannock County, Idaho (Yale and Stone, 1923). † Insoluble + SiO_2.

(23) Hydromagnesite (?) spring deposit in and upon shale, near Phillips Springs, Chiles Valley, Napa Co., California. R. C. Wells, analyst (Wells, 1910). The insoluble material is mainly shale.

(24) Coquina, Key West, Florida. F. W. Clarke, analyst (Clarke, 1924).

(25) Shell sand, John O'Groats, Caithness, Scotland. A. Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; Specimen No. SL-164). Contains (ppm) Ba 20, Cr 5, Li 10, Sr 1500 (R. L. Mitchell, analyst).

ANALYSIS NUMBER

	(26)	(27)	(28)	(29)	(30)			(31)	
					A	B	C		
SiO_2	0.22	0.20	17.0	19.44	10.73	0.08	10.65	Si	8.1
TiO_2	None		0.28	0.32	0.15	0.15	Trace	Al	3.9
Al_2O_3	0.21	0.28	9.0	5.71	3.69	1.16	2.53	Fe	5.0
Fe_2O_3	0.06		3.1	2.37	1.21	1.68	0.42	Ti	1.06
FeO				0.80					
MnO	Trace		0.18	0.15	0.05			Mg	1.6
CaO	50.19	52.84	37.0	35.62	42.22	41.68	0.54	Ca	23.9
MgO	0.66	0.82	3.4	1.74	0.34	0.10	0.24	Na	1.5
SrO	0.63	0.82	0.12					K	0.71
BaO			0.024					Sr	0.093
Na_2O			2.5	2.06	1.87			Ba	0.078
K_2O			1.1	0.91	1.47			B	0.032
P_2O_5	Trace			0.06	0.22			Mn	0.12
CO_2	40.60	41.60	33.9‡	(27.52)	21.72			Ga	0.0013
H_2O (-)	0.79	0.24		(1.35)				Ni	0.009
H_2O (+)	5.86				12.06			Cu	0.008
Org. Matter		0.16*		(0.70)	0.03			Co	0.001
SO_3	0.51	0.29†		0.30	0.43			Cr	0.019
Ign. loss				31.74				V	0.041
N				(0.03)				Zr	0.010
Cl				(1.84)**					
NaCl					2.36				
Total	99.73	97.25	107.8#	100.42	99.25				

(26) Calcareous bottom mud, Bahamas. E. T. Erickson, analyst (Wells, 1937). The organic content of Bahaman bottom mud, apparently not the same sample, as determined by Erickson is total organic C, 0.65%; N, 0.07%; P, 0.01%; stabilized organic C insoluble in acids, 0.19%; stabilized organic H insoluble in acids, 0.03%.

(27) Calcareous sediments rich in *Halimeda* debris, from 108-foot depth in Bikini lagoon. Analyst A. C. Vlisidis; flame photometer determination of SrO by W. W. Brannock (Emery et al., 1954). * Acid-insoluble organic. † Acid-soluble SO_3.

(28) Foraminiferal lutite, top of core A179-4 at depth 2965 meters, 16° 36' N, 74° 48' W, off the SW coast of Haiti. 0-10 cm. C^{14} date is 3950 ± 250 years (Rubin and Suess, 1955). R. G. Smalley, spectrographer (Ericson and Wollin, 1956a). ‡ Loss on HCL-treatment; alkalimeter method. # Total includes 0.008% CuO, 0.18% V_2O_5, 0.018% Cr_2O_3, 0.06% B_2O_3, 0.008% PbO.

(29) Top of core 6-A18, North Atlantic, 49° 03' 30" N, 32° 44' 30" W, contains 0.1 ppm Se (Edgington and Byers, 1942). **Oven-dry basis. Dried salts from sea water were not removed.

(30) *Globigerina* ooze, *Meteor* station 304 (Correns, 1937), Brünger, analyst. (A) Whole sample; (B) Soluble after digestion for two hours in hot 20 percent HCl; (C) Insoluble residue.

(31) Average chemical composition of Pacific core NH-9, 21° 41.2' N, 157° 28.5' W, depth 3027 meters, *Globigerina* ooze containing abundant pyroclastic material (Goldberg and Arrhenius, 1958).

	ANALYSIS NUMBER				
	(32)	(33)	(34)	(35)	(36)
SiO_2	22.30	0.05	0.05	0.05	8.40
Al_2O_3	0.42		0.06	0.11	1.31
Fe_2O_3		0.85			Trace
MnO		0.13			
CaO	40.19	54.15	55.34	52.46	46.83
MgO	0.14	0.87	0.26	0.90	3.54
Na_2O		0.18		0.33	0.48
K_2O				0.71	0.22
Li_2O					Trace
P_2O_5		0.12	Trace		Trace
NaCl			0.03	1.45	
CO_2	31.58	42.15	42.78	40.88	38.20
H_2O (-)		0.15	1.37	1.02*	1.71
H_2O (+)					
Cl		0.07			
SO_3	0.14	0.28	0.32	1.82	
Ign. loss	5.87				
Org. Matter		0.92			
Org. C			0.04	0.30	
Org. H			0.02		
Total	100.64	99.92	100.27	100.03	100.24

(32) Limestone caprock, Pleistocene age, Lubbock, Lubbock County, Texas. J. E. Stullken, analyst (Schoch, 1918).

(33) Caliche, Buliba-ha, Chiapas, Mexico; F. Roel, analyst (Instituto Geologico Mexico, 1913).

(34) Calcareous tufa, Mammoth Hot Springs, Yellowstone National Park. F. A. Gooch, analyst (Clarke, 1915).

(35) Travertine from cavity near Pulsating Geyser, Mammoth Hot Springs, Yellowstone National Park. J. E. Whitfield, analyst (Clarke, 1915). * Includes H of organic matter.

(36) Calcareous tufa, main terrace, Redding Spring, Great Salt Lake Desert. Analyst, R. W. Woodward, (King, 1878, p. 502).

	ANALYSIS NUMBER					
	(37)	(38)	(39)	(40)	(41)	(42)
SiO_2	0.40	1.13	0.75	0.80	14.25	1.57
TiO_2			0.03		0.40	
Al_2O_3	0.52	0.51	0.25	0.01	5.95	0.40
Fe_2O_3	0.08	0.31	0.64		4.01	0.24
MnO		0.02		Fe 0.04	Trace	
CaO	54.70	55.07	52.30	55.10	37.35	53.54
MgO	0.60	0.52	2.14	0.44	1.79	1.02
Na_2O	0.16		0.01		0.57	
K_2O	0.00		0.04		0.62	
P_2O_5		0.020		P 0.04		0.007
CO_2	41.70	(42.57)	43.54	43.29	29.56	
H_2O (-)			} 0.50		1.16	0.06 (105°C)
H_2O (+)					4.14	
S	0.27*			0.02	0.97	0.007
SO_3	(0.05)	0.07				
Ign. loss	(43.00)	43.15				43.27
Org. Matter	Trace					
MnO_2						0.02
Total	98.43	100.80	100.20	99.76†	100.77	100.13_4

(37) "Bedford oolitic limestone," Spergen Formation, Mississippian age, Bedford-Bloomington district, Indiana; oolites with foraminifera and small shell fragments as cores, frequently cross-bedded. Alice W. Epperson, analyst (Bur. Standards Tech. Paper 349, 1927; cited in Loughlin, 1930).
* Total S.

(38) Oolite of the Ste. Genevieve Formation, Mississippian age, Hardin County, Illinois. L. D. McVicker, analyst (Lamar, 1957).

(39) Oolite with foraminiferal centers, upper Sarmatian (Tertiary) age, upper Ilz valley, eastern Styria, Austria (Hübl, 1942).

(40) Fine-grained algal Curley Limestone, Utah (Proctor and Clark, 1956). †Total includes 0.01% Cu, 0.01% Pb.

(41) Rock consisting of fine-grained calcite particles coated by limonite, together with an assemblage of foraminiferal and ostracodal tests indicating deposition in shallow water, perhaps brackish water (Hubl, 1942).

(42) Average of ten analyses of channel samples of fine-grained, brackish water limestone, containing charophyte oogonia and ostracodes and made up of crusts like those produced by blue-green algae, Baum Member, Paluxy Formation of Lower Cretaceous age, Ravia-Mannsville area, Oklahoma. T. E. Hamm and A. L. Burwell, analysts (Wayland and Ham, 1955).

	ANALYSIS NUMBER					
	(43)	(44)	(45)	(46)	(47)	(48)
SiO_2	6.30	0.10	1.45	0.29	0.40	0.52
TiO_2	0.05	0.04	0.03			
Al_2O_3	0.75	0.14	0.74	0.26	0.37	Trace
Fe_2O_3	0.39	0.08	0.45	0.11	0.24	0.13
FeO						
MnO	0.05		0.04	0.005	0.013	Trace
CaO	51.09	54.35	53.52	55.53	55.88	54.81
MgO	0.63	0.93	0.60	0.70	0.38	0.39
Na_2O	0.07		0.12	0.07		
K_2O	0.13		0.16	0.02		
P_2O_5	0.03		0.03	0.046	0.011	0.02
CO_2	40.22		42.40	(43.42)	(43.62)	43.18
H_2O (-)	0.08 (105°C)		0.07			0.03
H_2O (+)						
Ign. loss	(40.35)	43.92	(42.82)	43.23	43.35	
SO_3				0.15	0.15	
S						Trace
FeS_2	0.04		0.14			
Insol. res.	(7.98)		(2.82)			
Total	99.83	99.56	99.75	100.41	100.79_4	99.08

(43) Turbid fine-grained carbonate containing numerous pellet structures, and recrystallized along a diffuse network of channels to anhedral carbonate of 0.03-0.1 mm. grain size. Upper Old Red Sandstone Series, Devonian age, near Muirkirk, Ayr, Scotland. A. Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; Specimen No. SL-170). Contains (ppm) Ba 15, Cr. 15, Li 20, Pb 15, Sr 250 (R. L. Mitchell, analyst).

(44) Average of 8 analyses of reef, fine-grained to foraminiferal and crinoidal, in the Marble Falls Formation of Pennsylvanian age in Burnet County, Texas (Barnes, 1952).

(45) Limestone, Oil Shale Group, Calciferous Sandstone Series, Carboniferous age, Waterbeck, Dumfries, Scotland. Compact limestone composed of fragments of shells, polyzoa, foraminifera, productid spines, *Calcisphaera* and ostracodes cemented by fine-grained calcite and recrystallized small organic fragments. A. Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; Sample No. SL 143). Contains (ppm) Ba 10, Li 26, Sr 200, V 20 (R. L. Mitchell, analyst).

(46) Crinoidal and bryozoan fragments in a matrix of broken fronds of fenestellid bryozoa, Salem Formation, Mississippian age, Union County, Illinois. L. D. McVicker, analyst (Lamar, 1957).

(47) Lithographic limestone, St. Louis Formation, Mississippian age, Madison County, Illinois. L. D. McVicker, analyst (Lamar, 1957).

(48) Dense subcrystalline, conchoidally fracturing Mosheim Limestone of the Middle Stones River Group of Ordovician age, Pendleton Co., West Virginia (McCue et al., 1939).

	ANALYSIS NUMBER					
	(49)	(50)	(51)	(52)	(53)	(54)
SiO_2	1.15	20.01	12.91	21.61	8.40	39.44
TiO_2				0.08	0.20	0.15
Al_2O_3	0.45	1.23	0.98	1.51	0.70	1.01
Fe_2O_3		0.76	0.43	1.23	1.15	0.86
FeO	0.26				0.11	0.09
MnO		0.012	0.02	0.06	0.02	0.01
CaO	53.80	36.47	46.82	40.88	49.21	31.48
MgO	0.56	5.51	1.09	0.88	0.25	0.08
SrO		0.044				
Na_2O	0.07	0.09		0.07	0.21	0.29
K_2O		0.20		0.28	0.11	0.20
P_2O_5		0.083	0.17	0.07	0.58	0.65
CO_2	42.69	(34.18)	37.20	32.57	37.95	23.73
H_2O (-)	0.23		0.10	0.50 (105°C)	0.14	0.17
H_2O (+)	0.69				0.89	1.74
SO_3	None	0.78				
S			0.06			
FeS_2				0.01		
Ign. loss		34.70		(33.00)		
Insol. res.				(23.99)		
Total	99.90	99.88_9	99.78	99.76	99.92	99.90

(49) Lithographic limestone, Solenhofen, Bavaria. Analysis by G. Steiger (Clarke, 1924).

(50) Kinkaid Limestone, late Mississippian age, Johnson Co., Illinois. L. D. McVicker, analyst (Illinois Geol. Survey files). Finely disseminated, largely replacive silica, welded in considerable part into a coherent framework; carbonate matrix is mostly fine-grained, with some skeletal debris.

(51) Arenaceous crinoidal Coeymans Limestone of Devonian age, Pendleton County, West Virginia (McCue et al., 1939).

(52) Calmy Limestone, Carboniferous Limestone Series, near New Cumnock, Ayr, Scotland. Compact greenish-gray limestone composed of 0.02-0.03 mm grains of calcite and finer grained turbid interstitial siliceous material, with sporadic crinoid columnals and shell fragments. A. Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; sample SL-92). Contains (ppm) Ba 25, Cr 10, Li 15, Ni 10, Rb 30, Sr 500, Zr 15 (R. L. Mitchell, analyst).

(53) Silty limestone, La Caja Formation, late Jurassic age, Zacatecas, Mexico. Analyst, Alberto Obregón (Rogers et al., 1956).

(54) "Highly calcareous siltstone," La Caja Formation, late Jurassic age, Zacatecas, Mexico. Analyst, Alberto Obregón (Rogers et al., 1956).

	ANALYSIS NUMBER					
	(55)	(56)	(57)	(58)	(59)	(60)
SiO_2	12.65	26.33	36.65	38.00	55.90	55.42
TiO_2	0.00	0.05		1.23	0.20	
Al_2O_3		0.82	0.91+2.12*	25.22	19.92	22.17
Fe_2O_3		0.66	0.82	17.53	7.30	8.30
FeO	0.91		7.54†	0.27	0.39	Trace
MnO	0.00	0.06		Trace		
CaO	46.97	39.45	39.50†	2.07	0.50	0.15
MgO	0.56	0.95	7.23†	1.31	1.18	1.45
SrO	0.00					
Na_2O	0.00	0.15		0.58	0.23	0.17
K_2O	0.00	0.27	0.03	2.99	4.79	2.32
P_2O_5	0.00	0.02	3.90‡	Trace	0.10	
CO_2	(37.85)	30.85		2.35	0.38	
H_2O (-)		(105°C) 0.48	0.62	2.41	2.54	2.10
H_2O (+)				7.04	6.52	7.76
Ign. loss	38.60	(30.50)				
S	0.00					
Insol. res.		(27.78)				
FeS_2		0.04				
C	(0.38)					
N	0.00					
Total	99.69	100.13	99.32	101.00	99.95	99.84

(55) Black siliceous concretions in Onondaga Limestone (Schwartz and Mathiasen, 1934).

(56) Subrounded quartz grains frequently secondarily enlarged with a low proportion of alkali-feldspar grains, cemented by large amounts of calcite. Upper Old Red Sandstone, Devonian age, Benarty Hill, Fife, Scotland. A. Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; sample SL-104). Contains (ppm) Ba 100, Cr 10, Li 8, Sr 500, V 30, Zr 20 (R. L. Mitchell, analyst).

(57) Greenish "sandstone" with abundant carbonate and phosphate cement, Lohne, Westphalia (von der Marck, 1855). * Insoluble and soluble Al_2O_3, respectively. † As carbonate. ‡ As $Ca_3(PO_4)_2$.

(58) Red earth cave sediment, residue from weathering of Schockekalke of Triassic age, near Weiz, Styria, Austria (Hübl, 1941).

(59) Residual clay from limestone, Staunton, Virginia. George Steiger, U. S. Geol. Survey, analyst (Clarke, 1924).

(60) Residual clay from Knox Dolomite, Morrisville, Alabama. Analyst, W. F. Hillebrand (Russell, 1889b).

	ANALYSIS NUMBER						
	(61)	(62)				(63)	(64)
		Sol. in 2% HCl	Insol. in 2% HCl	Insol. %	Computed Insol.* %		
SiO_2	14.11	0.07	4.34	54.2	56.2	25.05	19.10
TiO_2	0.16						Trace
Al_2O_3	4.16	0.06	1.69	21.1	17.5	8.28	2.86
Fe_2O_3	1.63	0.0	0.38	4.8	4.9	0.27	7.04
FeO		0.28	0.01	0.1	0.6	2.41	
MnO	0.038	0.02				4.11	
CaO	41.32	50.2	0.06	0.73	0.7	27.87	35.80
MgO	2.19	0.76	0.21	2.65	3.0	2.61	1.60
SrO	0.12						
Na_2O	0.39	0.03	0.05	0.66	0.65		
K_2O	0.71	0.06	0.39	4.9	4.5		2.05
P_2O_5	0.15	0.15				0.08	0.20
CO_2	33.53	40.3				24.20	30.20
H_2O (-)			0.36	4.5	5.1	1.44	1.10
H_2O (+)			0.5	6.3	6.1	2.86	
Cl		0.03					0.30
SO_3	0.04	Trace					
Ign. loss	(34.55)						
S	0.25						
MnO_2							0.05
C	0.61						
Total	99.40$_8$	92.0	8.0			99.18	100.30

(61) Argillaceous limestone, U. S. National Bureau of Standards sample 1a, dried at 105°C. (Nat'l Bur. Standards, 1954).

(62) Argillaceous Wellenkalk of the mu$_1$ zone, Muschelkalk (Middle Triassic), Plesse, West Germany, formed in an epicontinental sea apparently below wave base (Füchtbauer, 1950; personal communication). *Insoluble residue estimated from microscopic examination to contain 14.2% quartz, 5% plagioclase, 5.6% orthoclase, 75.2% illite.

(63) Highly calcareous Cretaceous age "shale," Mount Diablo, Calif. W. H. Melville, U. S. Geol. Survey, analyst (Clarke, 1924).

(64) Glauconitic limestone containing glauconite and quartz grains, molluscan, echinodermal, and foraminiferal remains, and fine-grained calcite cement; Lutetian (Eocene) age, from Conflans-Saint-Honorine (Seine-et-Oise) (Cayeux, 1935).

	ANALYSIS NUMBER					
	(65)	(66)	(67)	(68)	(69)	(70)
SiO_2	9.20	4.54	13.4	17.7		5.10
TiO_2			0.13	0.1		
Al_2O_3	7.48	0.94	2.73	2.5	0.64	3.78
Fe_2O_3		1.44	4.65	1.1	0.24	0.32
FeO	15.31					
MnO			0.20			0.06
CaO	29.51	47.84	55.7†	29.9	50.25	36.34
MgO		6.30	17.4‡	9.9		10.04
Na_2O				0.8		
K_2O				0.9		
P_2O_5	4.21	9.16	9.2	2.6	5.1	
CO_2	29.80		(25.9)	30.3	35.18	(33.11)
H_2O (-)	3.10*	0.08 (100°C)		0.6		
H_2O (+)						(0.52)**
SO_3	0.77			1.0		9.72
Ign. loss		29.90		(33.8)		
Total S			1.41			
Carbonaceous material				2.9		
"P.P.P."						34.27
Acid insol.					6.9	
F				0.3	0.50	
V_2O_5				0.1	0.01	
Org. oxygen						(0.46)
Total	99.38	100.20	104.8	100.7		99.63

(65) Greensand of Eocene age, Palestine, Texas. Analyst J. E. Stullken (Schoch, 1918).* H_2O plus organic.

(66) Phosphatic Cornishville horizon of the Perryville Limestone of Ordovician age, Harrodsville, Kentucky (Foerste, 1913).

(67) Fossiliferous crystalline limestone of the Sellersburg Formation, Devonian age, Clark Co., Indiana, containing abundant phosphate nodules (Murray, 1955). † $CaCO_3$. ‡ $MgCO_3$. R. K. Leininger, spectrographer. Total S, P_2O_5, and CO_2 chemically determined, under direction of M. E. Coller.

(68) Average chemical composition of 15 carbonate rocks of the Meade Peak Member of the Phosphoria Formation, Permian age, Coal Canyon, Wyoming (Gulbrandsen, 1958, compiled from McKelvey et al., 1953).

(69) Phosphatic limestone of the La Caja Formation, Jurassic age, Zacatecas, Mexico. Analysts, Guttag, Caemmerer, Barlow, Rowe and Tucker (Rogers et al., 1956). Highly variable amounts of phosphate pellets and replacements of radiolaria, in finely crystalline, strongly fetid calcite matrix, together with a little chert and detrital quartz.

(70) Anhydrite-containing dolomite of lower Tertiary age, southeast Ferghana USSR; a shallow-basin deposit. Analysis computes to 46% dolomite, 26% calcite, 16½% anhydrite, 9% terrigenous detritus (Osipova, 1949). **Hydrate water.

ANALYSIS NUMBER

	(71)	(72)	(73)	(74)	(75)	(76)	(77)			(78)
							A	B	C	
SiO_2	2.11		25.91	21.9 **	8.6	5.23	0.89	39.92	0.0	3.77
TiO_2	0.028		0.18		0.42	0.02				0.03
Al_2O_3	0.38		3.87	6.4††	4.6	0.29	0.20	8.76	2.7	0.78
Fe_2O_3	0.32		0.89	2.3**	2.6‡‡	0.61	0.04	14.41	23.9	2.20
FeO			0.73				0.41	1.01		
MnO	0.20		0.08		0.00	0.16				0.15
CaO	93.8*		17.89	21.2**	21.2	50.75	53.28	15.68	93.4	44.36
MgO	1.85†		10.44	8.4**	3.9	0.75	0.54	0.08	96.7	6.03
BaO			0.00							
Na_2O			5.57	1.0	0.42	0.08	0.07	1.56	51.5	0.06
K_2O			2.69	1.3	0.93	0.08				0.13
Li_2O			0.04							
P_2O_5	0.066	(<1)	0.04		0.44	0.11				0.04
CO_2		19.98	26.49	25.72		40.47	42.63	9.52	95.1	41.51
H_2O (-)		3.54	2.09			0.15 (105°C)				0.25 (105°C)
H_2O (+)		2.13	0.32							
Total S	1.1	16.71								
SO_3		(8.2)	0.00	0.5						
Cl		0.21								
Org. C		2.29		8.46						
Org. H		0.31		1.21						
N		0.04		0.29						
S			0.39	0.25	(1.2)					
O		0.00‡								
Org. matter		(2.64)$^{\alpha}$	2.23							
FeS_2						0.23				0.59
Vol. matter						(0.61)	0.43$^{\beta}$	7.94$^{\beta}$	61.0	
Ign. loss					55.3	(41.23)				(40.81)
Insol. res.						(6.08)				(5.33)
Ash		55.05#								
Total	99.85	100.05	99.91	98.93	99.41	98.93	98.49	98.88		99.90

(71) Coarse-grained fossiliferous limestone of Harrodsburg Formation, Mississippian age, Lawrence Co., Indiana, containing dark brown lenses and masses of gypsum throughout (Perry et al., 1954). *$CaCO_3$. †$MgCO_3$. R. K. Leininger, spectrographer. Total S and P_2O_5 chemically determined.

(72) Gypsiferous pyritic limestone of the Greenhorn Formation, Upper Cretaceous age, Black Hills area. Analyst, J. G. Fairchild (Rubey, 1930). ‡ Oxygen calculated by difference, probably a minimum value. # Ash minus CO_2 and SO_3 found in the ash. α H+C+N+O, probably a minimum value. The analysis computes to 45.4% calcite, based upon the CO_2 value, about 25.2% pyrite, 17.6% gypsum, <6.1% Fe oxides as limonite, >2.6% organic matter, about 2.0% bone phosphate, and 1.1% moisture. There is 0.03% chloroform-soluble material.

(73) "Oil shale," Green River Formation, Eocene age. John Hay, Jr., Well No. 1, Sweetwater County, Wyoming, J. J. Fahey, analyst (Unpublished data, U. S. Geol. Survey). Na_2O and K_2O determined by Laura Reichen using ion exchange method. Li_2O determined by Janet Fletcher by means of visible spectrum. Total includes 0.15 percent subtracted as oxygen correction for Cl and S, the S correction being made on the basis of the S present as pyrite. Spectrographic analysis by Janet D. Fletcher gives (ppm): Cu 380, Pb 20, Mn 500, Ni 20, Cr 30, V 60, Sc 2, Ti 90, Zr 30, Sr 900, Ba 500, B 70.

(74) Bed "J", Mahogany Ledge, Green River Formation, Eocene age, Rifle, Colorado (compiled from Stanfield et al., 1951). Consists principally of calcite, dolomite, illite, and kerogen. ** Ash composition calculated to raw-shale basis. †† (R_2O_3-Fe_2O_3).

(75) Bituminous stylolite filling in reef limestone of Pennsylvanian-Early Permian age, Horseshoe Atoll, West Texas. Analysis by U. S. Geol. Survey (Myers et al., 1956). ‡‡ Total Fe as Fe_2O_3.

(76) Burdiehouse Limestone, Oil Shale Group, Calciferous Sandstone Series, Carboniferous age, near Harburnhead, Midlothian, Scotland. Minutely granular calcite permeated by films of yellow bituminous matter, containing numerous ostracode shells and lesser amounts of pyrite, fossil phosphate, and (?) celestite. A Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; Sample SL-54). Contains (ppm) Ba 200, Li 3, Sr 1000 (R. L. Mitchell, analyst).

(77) (A) Buff Salem Limestone, Mississippian age, (B) Residual clay of associated stylolite seam, (C) Percentage of each constituent lost in going from (A) to (B) (Stockdale, 1922). K. W. Ray, analyst. β Volatile and combustible matter, less CO_2.

(78) Limestone, Cementstone Group, Calciferous Sandstone Series, Carboniferous age, near Riccarton Junction, Roxburgh, Scotland. Large fairly thin-walled shells in calcite mudstone showing a pellet-like structure and containing shell fragments coated with oolitic carbonate as well as fragments of shelly calcite mudstone, the whole in places partly recrystallized and dolomitized. A. Muir and H. G. M. Hardie, analysts (Geol. Survey Gt. Britain, 1956; Sample No. SL-200). Contains (ppm) Ba 15, Cr 5, Li 30, Rb 30, Sr 250 (R. L. Mitchell, analyst).

	ANALYSIS NUMBER					
	(79)	(80)	(81)	(82)	(83)	(84)
SiO_2	0.06	15.40	0.31	0.41	32.28	0.49
TiO_2	0.00	0.20	0.005			
Al_2O_3	0.25	4.00	0.067	0.177	4.88	0.50
Fe_2O_3	0.02	0.58	0.084	0.157*	1.13	0.29
FeO	0.07	0.98				1.52
MnO			0.006			0.33
CaO	30.57	24.47	30.49	30.71	18.68	21.73
MgO	21.54	16.77	21.48	21.18	11.66	13.61
SrO			<0.01			
Na_2O	0.11	0.06	0.08	0.029	0.15	
K_2O	0.01	0.69	0.03	0.051	3.01	
P_2O_5			0.003	0.004		0.62
CO_2	(47.12)	36.32	47.25			31.45
H_2O (-)				0.11(105°C)	0.21(105°C)	0.09(105°C)
H_2O (+)						0.70
SO_3		0.16	0.035	0.031		
Ign. loss	47.74	(36.88)	(47.52)	47.26(105-950°C)	27.93	
S		0.26	0.013			
Insol. res.						(28.96)
C			0.08			
H_2			0.008			
Total	100.37	99.89	99.94	100.21_9	99.72	100.29

(79) Dolomitized reef-core, Racine Formation, Silurian age, Cook County, Illinois. Analyst, L. D. McVicker (Willman, 1943).

(80) Argillaceous off-reef dolomite, Niagaran Formation, Silurian age, Cook County, Illinois. Analyst, L. D. McVicker (Lamar, 1957).

(81) Dolomite, U. S. National Bureau of Standards sample 88, dried at 105°C. (Nat'l Bur. Standards, 1954).

(82) Dolomite of the Royer Formation, Cambrian age, Johnson County, Oklahoma, believed from textural and field relations to be a replacement of a highly pure marine limestone; cavities in outcrop samples such as this contain secondary calcite encrustations, not seen in quarry faces of fresh rock. A. C. Shead, analyst (Ham, 1949). *Total Fe as Fe_2O_3.

(83) Dolomite of the Honey Creek Formation, Cambrian age, Johnson County, Oklahoma, a sparingly fossiliferous marine unit containing brachiopod and trilobite fragments in some beds. Insoluble residue: typically 60% feldspar, 35% quartz, ~1% zircon and sericite, all detrital from a Precambrian area to the west, plus 1 to 15% glauconite. A. C. Shead, analyst (Ham, 1949).

(84) Fine-grained dolomite containing echinoidal and brachiopod fragments, angular to subangular quartz grains and streaks of chert, and accessory oolitic carbonate grains. Lower Cambrian age, near Chrudaidh, Kyle of Durness, Sutherland, Scotland (Geol. Survey Gt. Britain, 1956; Specimen No. M-2926). A. Muir and H. G. M. Hardie, analysts.

ANALYSIS NUMBER

	(85)	(86)	(87)	(88)	(89)	(90)
SiO_2	30.46	0.58	16.63	13.71	11.65	
TiO_2			0.40	0.21	0.01	
Al_2O_3	6.86	0.37	7.43	4.23	1.18	4.38‡
Fe_2O_3	4.53		0.28	1.19	0.25	
FeO	1.89		6.03*	2.79		
MnO			0.24	0.23		
CaO	16.02	25.18	21.62	27.41	4.87	4.62
MgO	10.07	18.11	10.20	12.20	37.66	35.40
SrO		7.86				
BaO		0.13	0.00			
Na_2O	0.38	0.11	0.14	0.23	0.31	0.63
K_2O	5.77	0.05	0.75	0.94	0.32	1.36
Li_2O			Trace		0.22	
P_2O_5		0.02	0.25	0.15		
CO_2	22.55	39.55	31.10	35.15	40.09	
H_2O (-)	1.42		0.67(105°C)	0.37	2.15	
H_2O (+)			2.61†		1.82	
Cl		0.04	Trace			0.65
SO_3		6.33	0.06		0.12	7.32
B_2O_3					None	
Org. Matter		0.92				
H_2S		Trace				
Ign. loss				(36.81)		
Vol. matter				(1.3)		
Insol. res.				(19.76)		
FeS_2			1.49	0.03		
C			0.64			
"P.P.P."						35.22
"Undet. res."						6.16
Total	99.95	99.25	100.54	98.84	100.65	95.74

(85) Unmetamorphosed dolomite of the Waterton Formation, Precambrian age, southern Alberta, containing some 40% by volume of disseminated authigenic potash feldspar crystals (Daly, 1917).

(86) Celestite-bearing dolomite of the Salina Formation, Silurian age, Maybee, Michigan (Kraus and Hunt, 1906). The alkaline earth precipitates were checked spectrographically to verify the separation of Ca and Sr.

(87) Ferroan dolomitic siltstone, Middle Coal Measures, Woodborough bore hole; tough, dark gray, unbedded rock consisting of an aggregate of 5-10μ carbonate rhombs having n_O = 1.680-1.705, with tiny, angular grains of quartz and clay minerals, small pyrite streaks, a little collophane, and coloring from carbonaceous material. G. A. Sergeant, analyst (Edwards and Stubblefield, 1948). * Approximate because of presence of organic matter. † Includes any H_2O derived from organic matter.

(88) Compact gray rock composed mainly of grains of carbonate 0.005-0.01 mm across having refractive indices of ferroan dolomite, together with slightly larger grains up to 0.02 mm much altered to limonite (probably were siderite). Cementstone Group, Calciferous Sandstone Series, Carboniferous age, near Mid Calder, Midlothian, Scotland. A. Muir and H. G. M. Hardie,analysts (Geol. Survey Gt. Britain, 1956; Specimen No. SL-181). Contains (ppm) Ba 2000, Co 15, Cr 30, Ga 5, La 30, Ni 30, Rb 300, Sr 200, V 60, Y 30, Zn 60 (R. L. Mitchell, analyst).

(89) Magnesite bed, Horse Spring Formation, Overton, Nevada. Charles Milton, analyst (Wells, 1937). An analysis of material from the same deposit by R. C. Wells (Wells, 1937) is very similar.

(90) Sedimentary magnesite rock of early Permian age, Western Urals (Frolova, 1955). ‡R_2O_3.

ANALYSIS NUMBER

	(91)		(92)		(93)	(94)
	Insoluble in water	Water-soluble	Acid-soluble	Acid-insoluble		
SiO_2	0.0		0.39	18.24		2.10
TiO_2			None	0.28		
Al_2O_3			None	5.90		2.82
Fe_2O_3	0.08		None	1.22	36.60*	24.00
FeO	9.02		42.10			3.62
MnO	0.12		0.61			1.12
CaO	0.0		0.24	0.75	0.87†	33.85
MgO	25.94		1.23	0.35	6.10‡	1.22
SrO						
BaO						
Na_2O		(Na) 12.41				
K_2O		(K) 0.06				
Li_2O		(Li) 0.09				
P_2O_5			0.33			0.34
CO_2	33.29				CO_3 57.03	30.30
H_2O (-)	0.0		0.58			
H_2O (+)						
Cl		19.06				
SO_3			None			
S				0.44		0.22
"P.P.P."			24.31			
Total	100.07		69.79	27.18	100.60	99.59

(91) Magnesite-halite rock, Unterbreizbach salt mine, Rhön region, Germany (Hartwig, 1955).

(92) Siderite-bearing bed, Devonian age, western Bashkiria. B. V. Bal'shina, analyst (Florenskij and Bal'shina, 1948).

(93) Caprock of Carlos Dome, Grimes Co., Texas, 3770-3780 foot interval in core. F. W. Jessen, analyst (Rolshausen, 1934). *Fe. †Ca. ‡Mg.

(94) Frodingham ironstone, Type D, of Mesozoic age; hard, calcite-cemented shell-rich limestone containing reworked oolites of chamosite largely replaced by limonite. Dried at 105°C. Analyzed by the Ore-mining Branch of United Steel Cos. (Taylor et al., 1952). Computes to about 28% limonite, 8% siderite, 5% chamosite, and 58% calcite.)

	ANALYSIS NUMBER			
	(95)	(96)	(97)	(98)
SiO_2	8.7	4.7	15.33	7.24
TiO_2			0.67	
Al_2O_3	8.3	4.4	11.56	6.11
Fe_2O_3	10.3	1.2	1.71	3.36
FeO	36.0	47.2	7.83	3.21
MnO	0.2	0.3	34.46	35.53*
CaO	5.3	4.7	2.29	11.30
MgO	3.8	2.6	3.37	2.30
BaO			0.07	
Na_2O			0.46	
K_2O			1.18	
P_2O_5	2.0	0.4	Nil	
CO_2	(22.2)	(32.9)	20.60	28.06
H_2O (-)			0.54	2.98
H_2O (+)			0.15	
S	(0.24)	(0.11)	Trace	
Ign. loss	25.3	34.1		
Total	99.9	99.6	100.22	100.09

(95) Northampton sand ironstone; chamosite oolites, partly replaced by limonite set in 0.03-0.2 mm grains of siderite formed by partial recrystallization of a finer grained siderite mud. Dried at 100°C, average of 4 analyses (Taylor, 1949). Computes to about 55% siderite and 27% chamosite.

(96) Northampton sand ironstone; compact fine-grained rock composed of over 80% siderite, together with some quartz. Dried at 100°C, average of 2 analyses (Taylor, 1949).

(97) Mn-rich carbonate bed of early Cambrian age, St. Tudwal's, North Wales (Mohr, 1956).

(98) Mn-rich beds, Green Band, Manuels, Newfoundland (Dale, 1915). * Includes 8.08% MnO_2.

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