ml glucose solution was given. As Fig. 2 shows, the urinary excretion of lanthanum^{140} rose rapidly once more. The short half-life of lanthanum^{140} (40.4 hr) resulted in low counting rates and large statistical errors so that the irregular shape of the excretion curve after the last infusion has no true significance.

When lanthanum^{140} was injected as the chloride instead of the EDTA, less than 5% of the injected dose was excreted through the kidneys over a period of 48 hr. However, subsequent calcium-EDTA infusions were equally effective in enhancing urinary excretion of lanthanum^{140}.

Although the response to calcium-EDTA infusions in promoting lanthanum^{140} excretion is quite definite, the *total* amount of lanthanum^{140} excreted is only of the order of 10–15%. It was found that shortening the time interval between injection of lanthanum^{140} as lanthanum-EDTA or lanthanum chloride and the subsequent infusion of calcium-EDTA increased the total lanthanum^{140} urinary excretion. In an effort to further enhance lanthanum excretion, calcium-EDTA was administered *simultaneously* with, and in part, even prior to the lanthanum^{140} EDTA infusion.

A "priming" dose of 3 g of calcium-EDTA in 300 ml glucose solution was infused in 2.5 hr and was followed by a 1.5-hr infusion containing 2 g of calcium-EDTA and 200 μc lanthanum^{140}-EDTA. The immediate urinary excretion of lanthanum^{140} was found to be rapid. Approximately 37% of the total activity was eliminated in the first day, about 30% being excreted in the first 4 hr as may be seen in the upper curve of Fig. 1.

These results are in qualitative agreement with decontamination studies using iron^{59} and yttrium^{91} (*7*, *8*). From the above results, as well as from current distribution studies in animals using lanthanum-EDTA and lanthanum chloride, it seems that the lanthanum in the lanthanum-EDTA complex can be replaced in significant amounts by physiological competitors such as calcium. Experiments with calcium^{45} as a tracer indicate that the calcium bound to EDTA is capable of prompt exchange with the calcium depots of the body (*2*). Therefore, it seems reasonable to assume that calcium exchanges also with lanthanum^{140}. The somewhat stronger bond formed by lanthanum with EDTA at physiological pH values does not rule out the possibility of calcium exchange by virtue of the law of mass action. Such an effect has not been reported for the lead-EDTA and yttrium-EDTA complexes, probably because of the greater affinity of these metals for the chelating agent.

The renewed excretion of lanthanum^{140} following the infusion of calcium-EDTA may be explained by the exchange of lanthanum^{140} for calcium; lanthanum which has been deposited in the bones and other tissues may thus once again form lanthanum-EDTA and be excreted. The equal effectiveness of calcium-EDTA infusions in promoting excretion of lanthanum following lanthanum chloride as well as lanthanum-EDTA injections would seem to support this hypothesis. When large amounts of calcium-EDTA and tracer amounts of lanthanum-EDTA are infused simultaneously, the increased amount of EDTA available for combination with lanthanum reduces the possibility of lanthanum remaining in ionic form and consequently the kidneys excrete more lanthanum in form of lanthanum-EDTA. Yet, even under these conditions, only 40% of the lanthanum is excreted and it would appear that, in addition, some irreversible binding or absorption of lanthanum occurs in the organism.

The fact that the effectiveness of lanthanum-removal by this chelating agent (EDTA) decreases with time, suggests its use as an investigative tool. Metals with different chelating tendency and affinities to body constituents (extra- or intracellular) will be removable in varying quantities, depending upon the specific properties, relative strengths, amounts, and time of administration of the complexing agents employed. That is, a given chelating agent will be effective only until the metal becomes physically or chemically unavailable. Furthermore, the prompt removal by chelating agents of excess radioisotopes subsequent to their administration in therapeutic doses suggests itself as a general method of changing the relative distribution, radiation efficiency and biological half-life of such isotopes. The use of chelating agents may thus permit the administration of isotopes of longer "physical" half-life to humans than has previously been considered safe.

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Colloidal-Size Silica in Sediments

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For many years students of sedimentation have questioned the role of colloidal silica in sediments. Most workers believe that dissolved silica is transported and precipitated in colloidal form. Very little is known about the amount of silica which is precipitated as a colloid. A recent study by Roy (*1*) indicates that silica in natural waters is in true solution, probably as an SiO_3^{2-} ion. In light of this study by Roy, the problem of chemical silica in sediments should be re-evaluated.

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The term chemical silica as used in this discussion means silica which is precipitated. The objectives of this paper are to show that chemical silica is present in large quantities in recent marine sediments and that many ancient clays and shales contain chemically precipitated colloidal-size quartz.

Chemical analyses of river and sea water and recent marine and ancient sediments are cited in many sources of geological literature. X-ray diffraction and differential thermal analysis techniques have led to some excellent mineralogical analyses of the colloidal fractions of recent marine sediments and ancient shales and clays. An analysis of these data is significant in evaluating the role of chemical silica in sediments. If silica has been and is being precipitated as a colloid and recrystallized as colloidal-size quartz, there should be colloidal-size quartz in recent marine sediments and inancient clays and shales. These sediments do contain appreciable quantities of colloidal-size quartz, as will be shown in this discussion.

Silica in river water and sea water. The concentration of silica in fluviatile waters has been reported by Clarke (*2*). He gave the following averages of the percentage of silica of dissolved solids in the fluviatile waters of the major continents:

Waters of North America	8.60
Waters of South America	18.88
Waters of Europe	8.70
Waters of Asia	9.51
Waters of Africa	17.89
General average	11.67

The concentration of silica in the dissolved solids in the river waters of South America and Africa is relatively high compared with the other continents. The tropical climate and weathering conditions are probably the major causes of the high concentration since these factors increase the effectiveness of removing the silica from the drainage areas. The silica content of the dissolved solids in the waters of the other continents is large, and only Ca, CO_3, and SO_4 are present in larger quantities. Clarke (*2*) estimated that 319, 170×10^3 tons of SiO_2 are added to the oceans annually from river waters.

The concentration of silica in the dissolved solids in ocean waters is much less than that which is present in the dissolved solids of fluviatile waters. Sverdrup (*3*) gave no value for the SiO_2 as a dissolved solid in sea water, but in a table showing the elements present in sea water, he gave the value of silicon as 0.02–4 ppm. Clarke (*2*) observed, in regard to the small amount of silica in ocean waters, that "Silica is assumed to be wholly thrown down, the trifling residue held in solution being negligible."

Utilization and precipitation of silica. A tremendous quantity of silica is added to the ocean annually. This indicates that the silica is utilized or precipitated when the fluviatile waters enter the ocean since there is such a small amount present in sea water. The main portion of this discussion is concerned with some of the possibilities of utilization and precipitation of silica when it is brought into the marine environment. Some of these possibilities are as follows: (1) The silica may remain in solution or suspension. (2) The silica may be utilized by marine organisms. (3) The silica may combine with another colloid and be precipitated as a silicate with the excess colloidal silica subsequently crystallizing as colloidal size quartz. (4) The silica may be precipitated to form a relatively pure siliceous sediment. These 4 possibilities will be discussed in more detail and each will be analyzed for its relative merits.

If the silica which is carried to the oceans remained in solution or suspension, there would be much more in sea water than is now present. The silica now present in solution in sea water must be in equilibrium with respect to sea water, otherwise the amount would increase continually. Enough silica probably remains in solution to maintain this equilibrium, and the rest must be precipitated or utilized by marine organisms.

Marine organisms, especially diatoms and radiolarians, use silica as the structural constituent of their tests. These animals are planktonic types and live in areas in the open sea where the silica is present in very small amounts, which indicates that there is enough present under normal equilibrium conditions in sea water to sustain the needs of these animals. Rankama and Sahama (*4*) indicate that the difference in the amount of silica in the dissolved solids of fluviatile and sea water is due to its utilization as a structural constituent in shells of certain marine organisms. They state also that "There is no evidence of inorganically precipitated silica in recent marine sediments and, therefore, the inorganic deposition of silica in sea water is geochemically unimportant." The authors believe that a large quantity of the silica present in recent marine sediments is inorganic in origin. This is difficult to prove but, as will be shown later in this discussion, the data on the amount present, the content of sea water, and the habitat of most siliceous organisms are all factors which support the observation that much of the silica is inorganic in origin.

A third possibility is that the silica which is carried to the sea, either in solution or in colloidal suspension, may combine with some other colloid or ion to form a silicate. This would seem to be a reasonable hypothesis since colloidal silica and the SiO_3 ion are both negatively charged. A combination with some positive colloid or positive ion could result, and during diagenetic changes produce a silicate. Aluminum hydroxide is a positive colloid and ferric hydroxide can be either positive or negative. It seems plausible that the colloidal silica could combine with aluminum hydroxide or ferric hydroxide to form clay minerals and iron hydroxides. After these negative colloids have been satisfied, the excess colloidal silica could form colloidal-size quartz. Buckley (*5*) gives reference to the fact that the relationships of size and solubility may produce a very small particle which does not tend to grow larger. If the dispersion of the colloid is great and the solubility very small, this situation described

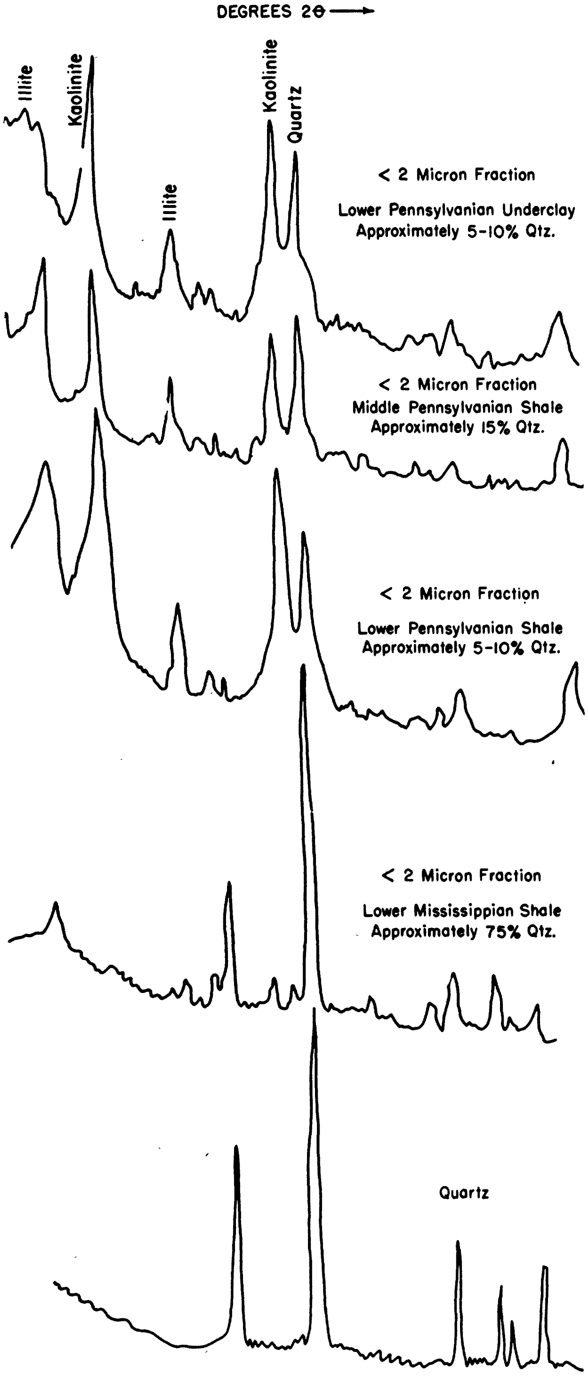

FIG. 1. Some x-ray spectrometer traces of clays and shales showing the approximate quantity of colloidal silica.

by Buckley may be produced and thus explain the presence of colloidal-size quartz in ancient sediments.

Data on colloidal quartz in sediments. Revelle (*6*) found, in his studies of some bottom samples of the Pacific, that x-ray powder photos of the colloidal fractions of all samples yielded diffraction lines identical to those of the mineral quartz.

Correns (*7*) in his work on the sediments of the Equatorial Atlantic Ocean, analyzed the fine fractions by x-ray methods. His analyses of the <1 μ fraction show quartz present in the great majority of the samples and in the majority of cases in amounts from 10–50%. This would seem to substantiate the hypothesis that there is a large quantity of silica in the form of the mineral quartz in the colloidal range.

In the study of some recent sediments of the Pacific Ocean, Grim, Dietz, and Bradley (*8*) found that quartz was present in the < 1 μ fraction of almost every sample. They estimated that there was 5–10% quartz in the 1–0.1 μ fraction and from 1–2% in the < 0.1 μ fraction.

There have been very few mineralogical analyses of the fine fractions of recent marine sediments, but the data which are available in the literature show that there is a substantial quantity of colloidal quartz.

In ancient clays and shales, quartz is present in the < 2 μ fraction of almost every clay or shale of Paleozoic age that the authors have analyzed (Fig. 1). This indicates that colloidal quartz may be an important constituent in ancient clays and shales.

Johnson (*9*), in a study of the insoluble residues of some limestones of Indiana, found that quartz was present in all the fine-size fractions and that it usually was the main constituent. This may mean that in a chemical sediment such as a limestone, colloidal silica may be precipitated and later crystallize to colloidal-size quartz.

The average chemical analysis of shale (*2*) reveals that there is 58.10% SiO_2. Mason (*10*) states that argillaceous rocks with more than 50% SiO_2 generally contain free silica. Although some of the quartz is present as detrital grains in the silt fraction, much of the quartz in the clay fraction is the result of colloidal silica deposition and from this a crystal formation to colloidal-size quartz.

The average chemical composition of 235 samples of Mississippi delta sediments (*11*) reveals that there is 69.96% SiO_2 and 10.52% Al_2O_3. The delta sediments are higher in silica than the average shale, as would be suspected since the silica probably is precipitated along with some clay minerals on the delta as soon as it comes into contact with sea water. There is the problem of spreading the precipitated silica to other areas of the ocean floor by currents, and density or turbidity currents could carry the silica to the pelagic and abyssal zones of the ocean bottom.

The data in the preceding paragraphs indicate that a considerable quantity of colloidal-size quartz is present in both recent and ancient sediments. It seems reasonable that most of this colloidal-size quartz is deposited by inorganic chemical precipitation from solution or by flocculation of colloidal silica when it comes in contact with ions or electrolytes in sea water.

Deposition of siliceous formations. The writers will not attempt to review the literature pertaining to the origin of cherts. An excellent summary of the more important hypotheses for the origin of chert is given by Pettijohn (*12*).

From the preceding data, it seems probable that large amounts of silica are being and have been deposited in marine sediments, especially shales. If conditions are suitable, there could be a segregation of silica, either during weathering or during transport and deposition, whereby relatively pure siliceous deposits could be precipitated.

Much of the segregation could take place upon weathering. From a study on the weathering of a granite gneiss, Goldich (*13*) has indicated that the residual products contain much more alumina and less silica than the original rock. Mason (*10*) states, "From pH 5–9 the solubility of silica increases considerably, but alumina is practically insoluble. Under these conditions, removal of silica can take place, leaving alumina behind, as has been inferred during the formation of laterites and bauxites."

The pH of 5–9 is a common pH of present-day streams and silica would, therefore, be predominant over alumina. This is borne out from the data by Clarke on analyses of river water which were given before in this discussion.

In order to obtain a clean separation of silica, the land in all probability must be in a state of low relief. Under conditions of low relief it would be possible to have a mantle of residual material which would retain the alumina and iron and contribute relatively large quantities of silica to fluviatile waters. It is believed that relief is a very important factor in the formation of siliceous deposits. This is not a new idea. Moore and Maynard (*14*) stated, "At the present time the greater portion of the silica entering sea water is being deposited with the clays and silts, but at times of peneplanation, when chemical denudation is at its maximum, the silica as well as other chemical precipitates might form pure deposits."

When the silica, which is weathered under the conditions outlined above, is carried to the sea, it is in all probability precipitated or flocculated. The mechanism must be that the silica is precipitated by the presence of large amounts of electrolytes or ions in sea water. If Fe^{+++}, Al^{+++}, or some other highly charged cation or positive colloid were present, it is possible that it would be attracted to the SiO_3 ion or to the negatively charged colloidal silica and cause precipitation or flocculation to form clay minerals. A small amount of a highly charged cation could precipitate a large quantity of silica. During diagenesis the excess silica could be released from the complex to form colloidal-size quartz.

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Diethyl 2-chlorovinyl Phosphate and Dimethyl 1-carbomethoxy-1-propen-2-yl Phosphate—Two New Systemic Phosphorus Pesticides

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The use of organic phosphates as pesticides has increased rapidly since their discovery by Gerhard Schrader (*1*) in Germany immediately prior to World War II. Following this, Schrader proceeded to demonstrate the activity of certain of these as systemic poisons: poisons taken into and transported through the plant. Much additional work has been done by other workers since Schrader's discovery.

During an investigation of certain new organic phosphorus compounds at the Shell Agricultural Laboratory, 2 have given outstanding results when used as systemic poisons and as fumigants. The 2 organic phosphorus compounds are diethyl 2-chlorovinyl phosphate (distils at 116° C at 10 mm) and dimethyl 1-carbomethoxy-1-propen-2-yl phosphate (distils at 106–7.5° C at 1 mm).

The systemic activity of the two new compounds was measured by a root absorption technique. In this test the materials are diluted to the desired ppm of toxicant in water from a 1% by weight acetone solution. This dilute solution is placed in a 250-ml Erlenmeyer flask and a pinto bean plant with 2 primary leaves and with roots washed free of soil is placed in the flask. A gas barrier of nonabsorbent cotton is placed in the neck of the flask around the stem of the pinto bean plant to prevent fumigation effects from volatile compounds. The pinto bean plant has been infested previously with 2-spotted mites, *Tetranychus bimaculatus,* Harvey. Mortality counts are made 48 hr after introduction into the flask. Two compounds that have systemic activity and are in commercial use were used as reference materials, i.e., Systox[1] (diethyl 2-mercaptoethyl thionophosphate) and OMPA[2] (octamethylpyrophosphoramide).

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[2] Monsanto Chemical Company, St. Louis 4, Mo.