SILICA IN NATURAL WATERS.

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ABSTRACT. The geological literature relating to the transportation and precipitation of dissolved silica is essentially unanimous as to the colloidal state of the silica.

The present paper reviews the geological literature with special reference to the basis for this conclusion. It is shown that the conclusion is based on inadequate chemical evidence. Recent chemical investigations which indicate that the dissolved silica in natural waters is in true solution, probably ionic, are cited.

As the prevailing theories on the origin of the siliceous sedimentary rocks are based on the assumption that the dissolved silica is colloidal, it is felt that knowledge of the overwhelming evidence to the contrary should clarify our geological thinking on these perplexing problems.

INTRODUCTION.

DURING the past ten years the author has made rather extensive studies of chert in a variety of areas and geologic systems, but especially in the Mississippian limestone flanking the Ozark uplift. In attempting to arrive at a satisfactory explanation of field relationships I have found it necessary to examine the literature on the transportation of silica in natural waters. It has been found that there is a significant disagreement between the geologic and chemical literatures in regard to this subject. The present paper reviews each literature separately and presents what seem to be necessary conclusions.

The writer is indebted to numerous individuals, both geologists and chemists, who have discussed this matter with him. I wish to express my gratitude especially to Dr. F. B. Kniffen of Louisiana State University for his careful reading of the manuscript and to Dr. M. C. Schwartz, Director of the Engineering Experiment Station, Louisiana State University, for valuable assistance in the study of chemical literature and for his critical reading of the manuscript.

GEOLOGIC LITERATURE.

The geologic literature dealing with the transport of silica in natural waters considers the silica to be in a colloidal state. This concept has had profound effect on geologic thought regarding the origin of siliceous rocks.

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Nearly all subsequent discussions of the state of silica refer to a paper by Kahlenberg and Lincoln (1898)[11] * who remarked that their experiments seemed to indicate that silica in natural waters is colloidal. They examined the electrical conductivity and the effect on the freezing point of solutions of sodium, potassium, lithium, rubidium, and caesium silicates. These solutions were prepared by adding the required amounts of the pure alkali hydroxide to a solution of silicic acid. It was found that the alkaline silicate solutions thus formed were hydrolyzed into alkali hydroxides and colloidal silica. Calculations indicated that in a solution with less than one gram molecular weight of the silicate in 48 liters of water (1250 parts SiO_2 per million) the silica would be colloidal. After completing their chemical experiments, Kahlenberg and Lincoln found evidence in the literature that most natural waters contain very small amounts of dissolved silica. They therefore concluded without making a single analysis of natural waters that since the silica in the dilute solutions they had studied seemed to be colloidal, the silica in the even more dilute solutions (5 to 30 parts SiO_2 per million) in nature must also be colloidal.

This conclusion has been offered as sufficient proof of the colloidal state of silica in natural waters or as corroborative evidence to that effect by nearly every geologic author on the subject since 1900.

Clarke (1908, pp. 151-152)[3] makes the following statement: "In solution, according to L. Kahlenberg and A. T. Lincoln, sodium metasilicate is hydrolyzed into colloidal silica and sodium hydroxide; and this conclusion was also reached by F. Kohlrausch about five years earlier, although he stated it in a more tentative form. *In natural waters, then, silica is actually present in the colloidal state and not in acid ions.*" (Italics mine.) The same words are used in subsequent editions of the book in 1911, 1916, 1920, and 1924.[3]

Tarr (1917, p. 433)[22] accepts the idea that the silica in solution in streams is colloidal but does not refer to any supporting literature.

Van Tuyl (1918, p. 456)[29] comments that there may always be some dispute regarding the source of silica in chert but concludes ". . . that much, if not all, of the silica is of inorganic origin, having been deposited in the colloidal condition. . . ."

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* Complete references will be found at the end of this paper.

Gruner (1922, p. 442)[8] states: "It was formerly believed that silica was carried in solution as alkaline silicate and that on separation from the alkali the silica was precipitated,* but it is now held that silicates are hydrolyzed and that silica is carried as a colloid in dilute natural waters."* The asterisks indicate the locations of foot-note references. The first reference is to a paper published in 1913, the second to the paper by Kahlenberg and Lincoln[11] published in 1898.

Lovering (1923, p. 534)[15] says "So far as is known, silica is transported only in the colloidal state in natural solutions. . . ." He gives a footnote reference to the paper by Kahlenberg and Lincoln.[11]

Tarr (1926, p. 25)[23] "It has long been held by Kahlenberg and Lincoln,[11] Van Hise,[28] Leith and Mead,[14] and others that the silica was liberated (during weathering) as a definite silicic acid, but the view held at present is that it exists in solution as a silica sol, containing a varying quantity of water." Tarr is here more concerned with the true character of the colloidal silica than with the colloidal or non-colloidal state of the silica.

Moore and Maynard (1929, p. 302)[17] accept the conclusions of Kahlenberg and Lincoln and give the results of similar experiments, concluding ". . . complete hydrolysis of sodium silicate does not take place until a dilution of at least 25 parts per million silica is reached. . . ."

"It would appear, therefore, that silica in solution in natural waters is transported as a true colloid provided the concentration does not exceed 25 parts per million. . . ."

Twenhofel (1932, p. 44)[27] refers to the paper by Kahlenberg and Lincoln and concludes "It is probable, moreover, that the silicon dioxide indicated by analyses of the solid matter in solution in natural waters is really in the colloidal state and not in true solution." On page 510 he considers the matter at somewhat greater length, citing additional references including Moore and Maynard and concludes ". . . essentially all of the silica in natural waters may be considered to be in the colloidal state."

Tarr and Twenhofel (1932, p. 526)[24] accept the colloidal state of the silica transported in natural waters and consider the character of the colloid.

The foregoing review is not exhaustive. It does not include references to all authors who have accepted the colloidal state of the silica in natural waters, nor does it include references to authors who have preferred sources of silica other than surface or near surface natural waters. It is considered to be representative of American geological opinion regarding the state of silica in natural waters and probably also of British opinion.

CHEMICAL LITERATURE.

Chemical investigators have studied silica in solution rather extensively since the paper by Kahlenberg and Lincoln.[11] In general their investigations have been concerned with three major aspects of the problem.

1. The physical chemistry of alkali-silica-water systems.
2. The determination of silica in natural waters.
3. The removal of dissolved silica from natural waters in water purification, especially for boiler-feed purposes.

The study by Kahlenberg and Lincoln belongs in the first group. A more exhaustive investigation of the same type is found in a series of papers by Harman (1925-1926-1927)[9] on the system Na_2O-SiO_2-H_2O. As his conclusions are quite contrary to those of Kahlenberg and Lincoln they are presented here in some detail.

Harman investigated the conductivity, transport numbers, hydrolysis, sodium ion concentration, lowering of vapor pressure and freezing point, and heterogeneous equilibria in the system Na_2O-SiO_2-H_2O at 25° C. He studied the Na_2O-SiO_2 in ratios 2 : 1, 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, and 1 : 4 at concentrations of 2Nw to 0.005 Nw.

Conductivity measurements showed that ratios 2 : 1 and 1 : 1 are excellent conductors, whereas ratios 1 : 2, 1 : 3, and 1 : 4 are good conductors in dilute solutions but abnormally poor conductors in concentrated solutions. Harman indicated that hydrolysis into NaOH and colloidal silicic acid is not sufficient to account for the conductivity. Assuming the silicate ion SiO_3^{--} to be present, he calculated its mobility from the conductivity results. Later experiments on transport numbers checked this calculation and showed that ratio 1 : 1 ionizes to Na^+, OH^-, and SiO_3^{--}. In ratios 1 : 2, 1 : 3, and 1 : 4 the concentration of silicate ions is high but each ion contains more than 1 (SiO_2) per divalent charge, the average number of mols SiO_2 per divalent charge being equal to the ratio. In ratios 1 : 2, 1 : 3, and 1 : 4 the silicate ion is not simple SiO_3^{--} but is either an aggregation of simple silicate ions with or without colloidal silica or is a definite complex silicate ion.

Harman concluded from his freezing-point experiments that ratio 1 : 1 is the salt Na_2SiO_3 undergoing both hydrolytic and ionic dissociation. This process gives rise to the ions Na^+, OH^-, and SiO_3^{--} with some H_2SiO_3, the latter being crystalloid. Na_2SiO_3 is almost completely dissociated in dilute solution but only 27.8 per cent of it hydrolytically. Ratio 1 : 2 is the definite salt $NaHSiO_3$ behaving like Na_2SiO_3 and giving rise to Na^+, OH^-, $HSiO_3^-$ ions and crystalloid H_2SiO_3. Ratios 1 : 3 and 1 : 4 seem to be much more complex.

Harman concluded that SiO_3^{--} ions exist in all ratios up to 1 : 4. In ratios 1 : 1 and 1 : 2 the silica is all crystalloid in dilute solutions and in ratios 1 : 3 and 1 : 4 increasing percentages are colloidal. However, his conclusion which seems to have the greatest bearing here is that in extremely dilute solutions (0.005Nw) all of the silica in all ratios is crystalloid. Since 0.005 Nw, Harman's most dilute solution, is equivalent to 3.2 parts per million SiO_2 (Na_2O-SiO_2) which is of the same magnitude as the average content of natural waters, his conclusions would indicate that the silica in streams should be crystalloid, not colloidal.

Harman discussed in his fourth paper the results of Kahlenberg and Lincoln as well as those of other writers who favor colloidal silica and indicated fundamental errors in their assumptions and conclusions.

There is an extensive literature on the determination of silica in natural waters. Of particular interest here are papers relating to the colorimetric method and its response to colloidal and non-colloidal or crystalloid silica.

The colorimetric determination of silica seems to have been proposed by Jolles and Neurath (1898),[10] although it is commonly credited to Dienert and Wandenbulcke (1923).[6] See comprehensive, annotated bibliography in Schwartz (1938).[20]

Dienert and Wandenbulcke[6] describe the method and present results of the analyses of river waters. The test is made by adding 4 drops 1 : 4 H_2SO_4 to 50 cc. of water to be tested and then adding 2 cc. of 10 per cent solution of ammonium molybdate which produces a yellow color due to the formation of a complex silico-molybdate. This yellow color is compared with that of standard solutions to reveal the amount of silica present. Note: There have been numerous modifications of the method proposed because of interferences, etc., but the essential principles remain the same.

According to Dienert and Wandenbulcke, the importance of this test lies in the fact that it will not determine colloidal silica. It reacts only to silica in true solution. The authors explained that any colloidal silica present can be destroyed by adding .2 g $NaHCO_3$ per 50 cc. and heating on a water bath. They found, however, in their study of river waters that there was no detectable colloidal silica present.

In a later paper, Dienert and Wandenbulcke (1924),[7] describe the effects of alkaline solutions on colloidal silica. Their experiments indicate that in a two per cent sea-salt solution containing 120 milligrams of colloidal silica per liter, 88 mg. of non-colloidal silica is formed in seven days at 37° C., complete conversion occurs in six days at 41° C. or in two hours at 90° C. They point out, furthermore, that all neutral or alkaline solutions will act the same, whereas acid ones prevent conversion. They conclude from these experiments that the silica in natural waters is almost exclusively non-colloidal because alkaline salts dissolved in the water would convert any colloidal silica to the non-colloidal form.

Although the temperatures at which the experiments were conducted are somewhat above the temperatures of natural waters, time seems to be an equally important factor.

Harman (1927)[9] in the last of the seven papers already referred to discusses the colorimetric method. He used the method to analyse some of his solutions, and states that it will not determine colloidal silica.

The colorimetric method has been and is now widely used by biochemists and industrial chemists for the determination of silica in natural waters. Examination of their results shows that the quantities of silica indicated colorimetrically agree closely with those indicated by gravimetric methods. Many authors state that the colorimetric method will determine only silica in true solution or silica that is in the crystalloid state, although in more recent papers they seem to assume that there is no longer any question of this.

Industrial chemists who have investigated ways and means of removing dissolved silica from boiler feed water are unanimous that the silica is not colloidal. Schwartz (1938, p. 551)[21] reviewing this literature states: "Those investigators who have considered the problem experimentally have established the fact that silica can be, and is, present in the crystalloid state. Unpublished results obtained by the author with Mississippi River water at Baton Rouge, La., corroborate this finding. . . ."

Schwartz (personal communication, but see also bibliography 1934,[19] 1938,[20] and 1938[21]), investigating the silica content of the Mississippi River at Baton Rouge, Louisiana, made the following comparisons: first, water clarified and silica determined colorimetrically and gravimetrically; second, water clarified, ultrafiltered and silica determined by both methods. In neither instance was there any difference in the indicated silica content. The silica content of the Mississippi as determined by Schwartz (1938, p. 554)[21] is about seven parts per million, rarely varying more than two parts per million. This checks closely with earlier gravimetric analyses at New Orleans (11 parts per million) and Carrollon, La. (7 parts per million) reported by Clarke (1924, p. 80).[3]

Other quantitative studies using the colorimetric method may be found in papers by Atkins,[1] Lucas,[16] Thompson and Johnson,[25] Hazel King,[13] Earl King,[12] and Cooper.[5] In every case the results are comparable with average gravimetric analyses for the same or similar waters.

The author has found only one paper which questions the qualitative significance of the colorimetric method, Tourky and Bangham (1936).[26] Their results, however, are not sufficient to vitiate those of the authors already referred to.

Another indication that silica in natural waters is not colloidal has been presented by Rees.[18] He discussed the analysis of waters used in boilers by which the sodium and potassium were determined by difference and reported as sodium. Positive ions Ca, Mg, and NH_4 were determined, calculated into mille equivalents and totalled. Negative ions SO_4, NO_3, Cl, and CO_3 were treated likewise. The difference gave the amount of Na and K present. In some waters it was found that the positive ions were higher than the negative ions, a fact which suggested that some negative ion was present and not considered. The silica in the water determined colorimetrically and calculated as negative ions gave a sodium value by difference which checked very closely with the analytical value for sodium. In contrast to this is the conclusion of the chemists of the Water Resources Branch of the United States Geological Survey as stated by Collins, Lamar, and Lohr (1932, pp. 5-6).[4] "Its (silica) state in natural waters is not definitely known, but in reports of analyses it is assumed to be in the colloidal state, taking no part in the equilibrium between the acids and bases." This conclusion was stated again in almost the same words in a letter to the author by W. W. Hastings, chemist in the Survey laboratory at Austin, Texas, dated February 14, 1944.

SUMMARY.

The prevailing view on the part of geologists, that silica in natural waters is in a colloidal state, is based mainly on the work of Kahlenberg and Lincoln.[11] If, however, we are to extrapolate from experiments with alkali silicate solutions to conditions existing in natural waters, it is obvious that Harman's results,[9] based as they are on more elaborate and complete experiments, are more reliable than those of Kahlenberg and Lincoln. The results obtained by Harman indicate that the silica in natural waters is in solution as the silicate ion SiO_3^{--}.

The colorimetric method for the determination of silica, which has been shown by many authors to react only to silica in true solution, shows directly that the silica in natural waters is not colloidal. The close check between colorimetric and gravimetric values for silica in natural waters eliminates the possibility that only a part of the silica is ionized and detectable by the colorimetric method.

Additional chemical studies, such as the one by Rees[18] referred to above, further substantiate the view that the silica in natural waters is in ionic solution.

The experiments of Dienert and Wandenbulcke[7] seem to indicate that any colloidal silica present would in time become crystalloid because natural waters are prevailingly alkaline.

The ultimate distinctions between true solution and the colloidal state are the molecular size and atomic structure of the individual particles, and the chemical behavior of the substance in solution. In both regards, the available chemical literature indicates that the silica in natural waters is in true solution.

The character of the crystalloid silica particles in natural waters is not definitely known. Harman's experiments on electrical conductivity, ion mobility, and transport numbers indicate that there are a number of possible silicate ions. In the dilute sodium silicate solutions with Na_2O-SiO_2 in the ratio 1 : 1 Harman[9] concluded that all of the silica was in the form of the ion SiO_3^{--} and this, indirectly, favors a similar conclusion with regard to the silica in natural waters. Rees[18] assumed the ion SiO_3^{--} to be present and succeeded in balancing the acids and bases satisfactorily; however, another divalent silicate ion might have served as well. The solubility of silica in natural waters seems to be very sensitive to the pH value (Cooper, 1933).[5] It is likely that the nature of the ion is also affected by the pH value and will not be the same in all natural waters or remain the same in a given water which undergoes changes in pH value.

The desirability of additional research with respect to the actual molecular character of the dissolved silica and the ways in which the silica may be precipitated is obvious. To be of geologic significance, such research must be concerned directly with the silica in natural waters. The difficulties to be met in such investigations are also obvious. First, the extremely low concentrations of silica in solutions containing greater concentrations of more active ions. Second, the studies on precipitation must attempt to simulate the geologic environments in which the siliceous rocks are known to have formed. Some evidence relative to the precipitation of the silica can undoubtedly be found by the geologist in the field if he is not handicapped by preconceived notions about the state of the silica in natural waters or about the methods of its precipitation. The third, and perhaps the greatest difficulty, is that the geologist does not have the equipment, training, or the inclination to undertake such studies and the chemists are not sufficiently concerned with these matters.

CONCLUSIONS.

Chemical investigations, approaching the problem in a variety of ways, do not support the widely accepted concept that the dissolved silica in natural waters is colloidal. On the contrary, these investigations, to date, justify the following conclusions:

1. The dissolved silica in natural waters is in true solution or crystalloid rather than colloidal.

2. Although the molecular character of the dissolved silica has not been investigated directly, the evidence indicates that it is ionic.

REFERENCES.

1. Atkins, W. R. G.: 1926, Seasonal changes in the silica content of natural waters in relation to the phytoplankton. J. Mar. Biol. Assoc., vol. 14, 69.
2. ————: 1928, Seasonal variation in the phosphate and silicate content of sea water during 1926 and 1927, in relation to the phytoplankton. J. Mar. Biol. Assoc., vol. 15, 191.
3. Clarke, F. W.: 1908, The data of geochemistry. U. S. Geol. Survey Bulletin 330.
   1911—second edition, Bulletin 491.
   1916—third edition, Bulletin 616.
   1920—fourth edition, Bulletin 695.
   1924—fifth edition, Bulletin 770.
4. Collins, W. D., Lamar, W. L., and Lohr, E. W.: 1932, The Industrial utility of public water supplies in the United States. U. S. Geol. Survey, Water Supply Paper 658.
5. Cooper, L. H. N.: 1933, Chemical constituents of biological importance in the English Channel, November, 1930 to January, 1932, Part I: J. Mar. Biol. Assoc. of the United Kingdom, vol. 18, 694-699.
6. Dienert, F., and Wandenbulcke, F.: 1923, Determination of silica in waters. Comptes Rendues, vol. 176, 1478-1480.
7. ————: 1924, A study of colloidal silica. Comptes Rendues, vol. 178, 564-566.
8. Gruner, J. W.: 1922, The origin of sedimentary formations: the Biwabik formation of the Mesaba Range. Econ. Geol., vol. 17, 407-460.
9. Harman, R. W.: 1925-1926-1927, Aqueous solutions of sodium silicates. Jour. Phys. Chem., vol. 29, 1155-1168, vol. 30, 359-368, 917-924, 1100-1111, vol. 31, 355-373, 511-518, 616-625.
10. Jolles, H. and Neurath, F.: 1898, Colorimetric estimation of silica in water. Z. Angew. Chem., vol. 11, 315-316.
11. Kahlenberg, L., and Lincoln, A. T.: 1898, Solutions of silicates of the alkalies. Jour. Phys. Chem., vol. 2, 77-90.
12. King, E. J.: 1931, On the colorimetric estimation of silica. Contributions to Can. Biol. and Fisheries, Studies from the Biol. Stations of Can., N. S., vol. 7, 121-125.
13. King, Hazel: 1931, On the occurrence of silica in the waters of Passamaquoddy Bay region. Contributions to Can. Biol. and Fisheries, Studies from the Biol. Stations of Can., N. S., vol. 7, 129-137.
14. Leith, C. K., and Mead, W. J.: 1915, Metamorphic geology, Henry Holt and Co., New York, 13.
15. Lovering, T. S.: 1923, The leaching of iron protores: Solution and precipitation of silica in cold water. Econ. Geol., vol. 18, 523-540.
16. Lucas, C. C.: 1929, Further studies of the sea adjacent to the Fraser River mouth. Trans. Royal Soc. of Canada, vol. 23, 103-119.
17. Moore, E. S. and Maynard, J. E.: 1929, Solution, transportation and precipitation of iron and silica. Econ. Geol., vol. 24, 272-303, 365-402, 506-527.
18. Rees, O. W.: 1929, Occurrence of silicates in natural waters. Ind. and Eng. Chem., Anal. Ed., vol. 1, 200-201.

19. Schwartz, M. C.: 1934, Colorimetric determination of silica in boiler water. Ind. and Eng., Chem., Anal. Ed., vol. 6, 364-367.
20. ————: 1938, Silica in water. Louisiana State University, Bulletin 30, no. 14, 46 pages.
Contains an annotated bibliography of 69 papers on the subject.
21. ————: 1938, The removal of silica from water for boiler feed purposes. Jour. Amer. Water Works Assoc., vol. 30, 551-567.
Contains a bibliography of 107 titles, many of which are papers that consider the state of the silica.
22. Tarr, W. A.: 1917, Origin of the chert in the Burlington limestone. Am. Jour. Sci., vol. 44, 4th Series, 409-452.
23. ————: 1926, The origin of chert and flint. Univ. of Missouri Studies, vol. 1, no. 2.
24. ————, and Twenhofel, W. H.: 1932, Chert and flint, treatise on sedimentation, second edition, Williams and Wilkins, Baltimore, 519-546.
25. Thompson, T. G., and Johnson, M. W.: 1930, The sea water at Puget Sound Biological Station from September, 1928 to September, 1929, Publications, Puget Sound Biol. Station, 7, 345.
26. Tourky, A. R., and Bangham, D. H.: 1936, Colloidal silica in natural waters and the "silico-molybdate" color test. Nature, vol. 138, 587-88.
27. Twenhofel, W. H.: 1932, Treatise on sedimentation, Williams and Wilkins, Baltimore, 890 pages.
28. Van Hise, C. R.: 1904, Treatise on metamorphism, U. S. Geol. Survey, Mon. 47, 163.
29. Van Tuyl, F. M.: 1918, The origin of chert. Am. Jour. Sci., vol. 45, 4th series, 449-456.

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ERRATUM

"SILICA IN NATURAL WATERS," by Chalmer J. Roy. Vol. 243, July, 1945, pp. 393-403.

Through a printer's error the free valence of the SiO_3 ion is shown as one instead of two throughout the paper.