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SILICATE REACTIONS - A REVIEW

By A. G. Collins and Lillie R. Fisher

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CONTENTS

	<u>Page</u>
Abstract	3
Introduction	3
Analysis and classification.	4
Selected references	4
Buffering reactions.	8
Selected references	8
Diagenesis and weathering.	11
Selected references	12
Hydrothermal reactions	17
Selected references	17
In nonsaline media	17
In saline media.	30
Precipitation reactions.	32
Selected references	33
Solubility	43
Selected references	43
In nonsaline aqueous media	43
In saline aqueous media.	66
Corrosion prevention	82
Selected references	82
Author index	84
Title index.	92

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ABSTRACT

This review contains short discussions and annotated bibliographies of the following subjects related to silicate reactions: Methods of analyzing silicates, buffering in aqueous solutions, diagenesis and weathering, hydrothermal reactions in nonsaline and saline aqueous media, and corrosion prevention. An author index is included.

INTRODUCTION

Reactions of silica and silicate minerals are of interest to investigators of several scientific disciplines. Knowledge of the solubilities of silicates in saline and nonsaline aqueous media is vital in designing certain types of saline water desalination plants.

Silicate compounds can cause deleterious reactions in boilers. For example, boilers used in desalination can be damaged by silicate scale deposition. Boilers used in oil well steamflooding can be similarly damaged. Knowledge of silicate reactions is necessary to correctly treat boiler input waters.

Some silicate compounds inhibit corrosion of metals in boilers and pipes. A siliceous film is formed on the metal surface by adsorption.

Why silicates precipitate in one aqueous environment and dissolve in another aqueous environment is a basic chemical geological question. In one environment kaolinite might form, while in another environment serpentine might form. The solubilities of the clay mineral silicates is not well known. Why and how a clay mineral such as kaolinite alters in a certain aqueous environment is of interest to scientists concerned with water recovery, oil recovery, and recovery of other minerals.

For example, one form of kaolinite may be conducive to good water recovery from a given aquifer. Another form of kaolinite may allow even better water recovery, while a third form of kaolinite may allow no water recovery.

Several diagenetic, metamorphic, metasomatic, and weathering reactions involving silicates are not completely understood. The buffering effect of silicates in solution partially affects all of these occurrences. Considerable additional knowledge is necessary to understand all the reactions involved.

ANALYSIS AND CLASSIFICATION

Most of the following methods are for the determination of silica in aqueous solutions. Some of the methods can be used to distinguish colloidal from noncolloidal silica. Silicate minerals can be analyzed for 14 constituents using one of the methods (12).

A silicate mineral classification system is included (2). An electron micrograph study of silica rocks is shown (5).

Selected References

1. Aoki, F. Colorimetric Determination of Silica in Natural Waters.
2. Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.), v. 72, 1951, pp. 15-17.

A modification of the colorimetric phosphomolybdic method of measuring silica involves changing the yellow color to blue by means of reducing agents. Methods of dealing with certain reducing substances that occur in natural waters and interfere with the test are discussed.

2. Berman, H. Constitution and Classification of the Natural Silicates. Am. Miner., v. 22, No. 5, May 1937, pp. 342-408.

As the result of X-ray structural studies by Bragg and others, a new conception of silicate structure has evolved, and a new classification system. Evidence is presented for the validity of the newer concepts, and a detailed classification of hundreds of silicates is presented in tabular form. The classification is based on the various types of linkage of the silicon-oxygen tetrahedra found to be the fundamental motif of silica structures. The main divisions are the silica (three-dimensional networks), disilicate (sheet structure), metasilicate (chain structures or ring structures), pyrosilicate (double tetrahedra), and orthosilicate types (independent tetrahedral groups). The ratio of siliconlike atoms (which include Al or sometimes Be in part) to oxygen is 1:2 for the silica types; 2:5 for the disilicate types; 3:8, 4:11, or 1:3 for the chain-type metasilicates; $n:3n$ for the ring-type metasilicates; 2:7 for the pyrosilicates; and 1:4 for the orthosilicates.

3. Diénert, F., and F. Wandenbulcke. Determination of Silica in Waters. Compt. rend., v. 176, 1923, pp. 1478-1480.

A rapid method for determining noncolloidal silica with an accuracy of $\pm 2\%$ consists of adding 2 cc of 10% ammonium molybdate solution and 4 drops of sulfuric acid to 50 cc of aqueous sample and comparing the yellow color with that of 50 cc of a standard solution of sodium silicate or with a solution of 36.9 mg of picric acid per liter. Sixty milligrams of silica per liter is the maximum concentration that can be measured with 2 cc of ammonium molybdate solution. Colloidal silica can be included in the determination by first heating the solution in a platinum vessel with sodium bicarbonate. Colloidal silica is thereby converted to noncolloidal silica.

In most ordinary waters, silica exists in a noncolloidal state. Filtration of waters results in low values for silica content, because some silica is absorbed on the surface of diatoms.

4. Fresenius, W., and W. Schneider. Determination of Silicic Acid in Mineral Waters. Z. Anal. Chem., v. 207, No. 1, 1965, pp. 16-22.

In the colorimetric determination of silicic acid by the ammonium molybdate method, interfering molybdophosphates are removed by extraction with benzene and isobutyl alcohol. Polymeric silicic acid is converted to monomeric H_2SiO_3 by treatment first with HF and then with H_3BO_3 .

5. Iwao, S., H. Akabori, M. Koizumi, and H. Minato. Electron Micrograph of Some Silica Rocks, With Special Reference to the Micropores With Fluid Inclusions. Ganseki Kobutsu Kosho Gakkaishi (Journal of the Japanese Association of Mineralogists, Petrologists, and Economic Geologists), v. 37, 1953, pp. 167-178.

As the results of a preliminary study in the electron micrograph of the fractured surface of some silica rocks in Japan, such as coarse-grained vein-quartz and chalcedonic vein-quartz in silicified chert, highly silicified andesite by solfataric action, and chalcedonic sinter, it was revealed by the present authors that:

1. In the coarse-grained vein-quartz, the majority of fluid is carried in the micropores in crystals; in chalcedonic sinter, it is presumed to be involved in the interstices of ragged crystals, and in the chalcedonic vein-quartz, both in micropores and in interstices.

2. The usefulness of the decrepigraph on silica rocks depends upon the size of micropores, as well as upon the density of distribution of the micropores.

Further application of the electron micrograph of rock or crystal surfaces to the petrographic study is also suggested.

6. Iwasaki, I. Chemical Analyses of Some Components in Natural Water. Bunseki Kagaku (Japan Analyst), v. 3, 1954, pp. 508-516.

A review is given on determination of SiO_2 , Cl^- , SO_4^{--} , Ca^{++} , heavy metals, and radioactive elements.

7. Iwasaki, I., T. Katsura, and T. Tarutani. So-Called Silica Content of Natural Waters. Bull. Chem. Soc. Japan, v. 24, No. 5, November 1951, pp. 227-230.

By varying the method of analysis, the proportion of ionic, colloidal, and total silica content of hot spring, river, and sea water could be determined. It is necessary to analyze samples immediately after collection, since ionic silica coagulates over a period of time to produce colloidal silica. Natural waters contain some colloidal silica.

8. Kanie, T. Determination of Silica in High-Purity Water by an Ion-Exchange Method. Nagoyashi Kogyo Kenkyusho Kenkyu Hokoku (Res. Repts., Nagoya Municipal Ind. Res. Inst.), No. 27, 1963, pp. 35-38.

A mixture of water, HF, and Amberlite IRA 402 (OH-type) is shaken, the resin is filtered off, the Si is desorbed from the resin with H_3BO_3 and measured by the molybdenum blue method.

9. Mullin, J. B., and J. P. Riley. Storage of Sea-Water Samples for the Determination of Silicate. Analyst, v. 80, No. 946, January 1955, pp. 73-74.

Both acidified and unacidified filtered sea water stored in soda glass, Pyrex glass, and fused silica bottles for 8 weeks showed weekly increases in silicate content. The order was soda glass > Pyrex > fused silica. Acidification reduced the speed of solution except in the case of the fused silica bottle. Unacidified samples stored in polyethylene bottles showed constant silicate content after an initial loss during the first week; acidified samples showed no loss.

10. Rees, O. W. Occurrence of Silicates in Natural Waters. Ind. and Eng. Chem., Anal. Ed., v. 1, No. 4, Oct. 15, 1929, pp. 200-201.

Heretofore in the analysis of boiler water and surface water at the Illinois State Water Survey, the positive ions Ca^{++} , Mg^{++} , and NH_4^+ were measured and subtracted from the total of the negative ions $\text{SO}_4^{=}$, NO_3^- , Cl^- , and $\text{CO}_3^{=}$ to give a figure for Na^+ by difference. It was found that more accurate results were obtained if silicate ions were included with the negative ions.

11. Schink, D. R. Determination of Silica in Sea Water Using Solvent Extraction. Anal. Chem., v. 37, May 1965, pp. 764-765.

The colorimetric ammonium molybdate method of determining soluble silica can be applied to sea water by extracting acidified solutions of sea water with ethyl acetate, and measuring the absorbance of the ethyl acetate at 3,350 Å. The interference by phosphate is small. Turbid waters need not be filtered before analysis.

12. Suhr, N. H., and C. O. Ingamells. Solution Technique for Analysis of Silicates. Anal. Chem., v. 38, No. 6, May 1966, pp. 730-734.

A new solution technique makes possible the rapid and precise determination of most major and minor constituents of silicates in a single sample. Solution is effected by adding the melt of sample fused with lithium metaborate directly to cold dilute nitric acid that contains the internal standard cobalt. The solution is analyzed with an emission spectrometer using a rotating disk technique. Data for precision are given for the oxides of Si, Al, Mg, Ca, Sr, Ba, Ti, Mn, Fe, Cr, Cu, Zn, Zr, and Ni. Accuracy of the method is evaluated by comparison with chemical analyses of four rock samples. Na and K are determined on the same sample solution by flame photometry. The same solution can also be used to determine various elements colorimetrically, spectrographically, and by X-ray fluorescence spectrometry.

13. Tourky, A. R., and D. H. Bangham. Colloidal Silica in Natural Waters and the Silicomolybdate Colour Test. Nature, v. 138, Oct. 3, 1936, pp. 587-588.

It has been believed that in the determination of silica by Diénert and Wandenbulcke's colorimetric method using ammonium molybdate in acid solution, only the noncolloidal silica reacted to form a yellow color. Alkali treatment and ultrafiltration experiments indicate that colloidal silica also gives the color reaction and that most of

the silica in the river and well waters examined is colloidal in nature. The failure of the yellow silicomolybdate to pass through a relatively coarse ultrafilter indicates that the material may be an adsorption complex rather than a true heteropolyacid.

Determination of silica in sea water by Diénert and Wandenbulcke's method gives correct results if the silica has been in solution for a sufficiently long period of time.

14. Weitz, E., H. Franck, and M. Schrichard. Silicic Acid and Silicates. Chemiker Z., v. 74, 1950, pp. 256-257.

Orthosilicic acid, disilicic acid, and polysilicic acids of not too high a molecular weight can be distinguished from one another by the rate of formation of the yellow silicomolybdic acid. The rate increases from 75 seconds to 10 minutes to 1 hour, respectively, for the different forms. The high-molecular weight polysilicic acids do not produce a yellow color. The condensation of silica acids is reversible and is affected by pH, concentration, and temperature. River and well waters with as much as 50 ppm SiO_2 contain only orthosilicic acid. Hot springs contain up to 1,000 ppm SiO_2 as low-molecular weight silicic acids, including orthosilicic acid. Silicate minerals are studied by this method.

15. Zolotukhina, M. D. Determination of Small Amounts of Silicic Acid in Aqueous Solutions. Energetik, v. 13, No. 3, 1965, pp. 5-6.

The order of mixing the reagents affects the results obtained in the measurement of silicic acid by the molybdenum blue complex method.

BUFFERING REACTIONS

The pH of aqueous solutions is influenced by the buffering capacity of dissolved silicates. This effect is more pronounced in saline waters than in fresh waters.

Silicate buffering of saline water is important in surface and sub-surface bodies of water. Further research is needed to correctly interpret the total effect silicate buffering has upon modern and paleoenvironments.

Selected References

16. Garrels, R. M. The Role of Silica in the Buffering of Natural Waters. Science, v. 148, No. 3666, Apr. 2, 1965, p. 69.

In the oceans, dissolved silica and degraded silicates appear to participate in a reaction which fixes silica and alkali metal cations and releases hydrogen ions, resulting in the maintenance of the pH.

17. MacKenzie, F. T., and R. M. Garrels. Chemical Mass Balance Between Rivers and Oceans. *Am. J. Sci.*, v. 264, No. 7, Summer 1966, pp. 507-525.

The assumption of constancy of the chemical composition of ocean water requires that the excesses of dissolved constituents carried by streams to the ocean be removed. The chemical mass balance between streams and oceans is an attempt to evaluate this removal process, to see what reactions are necessary to accomplish this removal, and to maintain present ocean water composition.

Postulation of a steady-state model for the ocean leads to the removal of stream-derived dissolved solids as minerals in marine sediments, as dissolved constituents in sediment pore waters, and as materials cycled through the atmosphere. Disposal of the dissolved solids requires synthesis of typical clay minerals from degraded aluminosilicates before burial in sediments, by reactions of the type:

Such chemical, if not structural, synthesis implies control of the major ion ratios in sea water and the CO_2 pressure of the atmosphere by equilibria involving aluminosilicates. These "reverse weathering" reactions, by removing HCO_3^- and alkali metals from the oceanic system, prevent the ocean from attaining the composition of a soda lake. Also, chemical synthesis of typical clay minerals in the oceanic system implies that these minerals are in equilibrium, or nearly so, with an aqueous solution of the composition of average ocean water and should not be significantly altered upon entering the ocean as allogenic particles.

18. MacKenzie, F. T., and R. M. Garrels. Silica-Bicarbonate Balance in the Ocean and Early Diagenesis. *J. Sedimentary Petrol.*, v. 36, No. 4, December 1966, pp. 1075-1084.

If present stream discharge and dissolved load are assumed to be representative of the geologic past, and if the volume of the ocean has remained essentially constant, many problems arise concerning

the disposal of the dissolved constituents brought into the ocean by streams. Two of these problems relate to silica and bicarbonate.

The present rate of delivery of dissolved silica to the ocean would produce a much greater volume of sediment than is observed in the geologic column if all this silica were precipitated chemically or biochemically as "free" SiO_2 . The bicarbonate ion transported to the ocean must either be recycled through the atmosphere as CO_2 , or removed in carbonate sediments. Yet the precipitation of carbonate minerals, with concomitant loss of CO_2 to the atmosphere, leaves about 40 percent of the HCO_3^- unaccounted for!

These two problems can be solved by assuming that an acid-base reaction of the type

in which HCO_3^- is converted to CO_2 and recycled through the atmosphere, can account for the excess HCO_3^- and resolve the silica balance. Furthermore, we suggest that SiO_2 and HCO_3^- react with cations and the small, but significant, X-ray amorphous-Al-silicate fraction of the suspended load of streams according to reactions of the type

Reactions of this type may be considered "reverse weathering" and take place before deposition and burial. Chemical synthesis of compounds of the composition of chlorite, illite, and montmorillonite implies that these minerals are in equilibrium, or nearly so, with an aqueous solution of the composition of average sea water. Therefore, the bulk of these clay minerals should not be drastically altered upon entering sea water as allocthenic particles.

19. Weber, W. J., Jr., and W. Stumm. Buffer Systems of Natural Fresh Waters. J. Chem. and Eng. Data, v. 8, No. 3, July 1963, pp. 464-468.

The ability of natural fresh waters to maintain a closely constant pH is well recognized, but the interaction of buffer components lending this quality to natural waters is often not clearly defined. Discussion of the relative significance and of the interplay of the principal component systems of such waters is presented in an effort to describe more closely the nature of fresh water buffer capacity. Consideration is given the homogeneous-phase and heterogeneous-phase

chemical systems, and the biochemical and physicochemical activities common to most natural fresh waters. Appropriate emphasis is placed upon description of the mode of action of the carbonate system. Conceptual definitions of alkalinity and acidity are presented, and their respective roles in providing buffer action is discussed. Rigorous mathematical expressions for acid-base titrations and buffer capacities in carbonate systems are derived from consideration of conditions of electroneutrality and mass law relationships. A method for simultaneous graphical representation of systems of logarithmic equations treating chemical equilibria is presented as a means for facilitating the survey of equilibrium relationships and their respective dependencies upon control variables such as pH.

20. Weber, W. J., Jr., and W. Stumm. Mechanism of Hydrogen Ion Buffering in Natural Waters. J. Am. Water Works Assoc., v. 55, No. 12, December 1963, pp. 1553-1578; Correction: *ibid.*, v. 56, No. 4, April 1964, p. 386.

The pH of ocean waters is greatly affected by dissolved buffering agents, including the carbonates, silicates, phosphates, and, to a lesser extent, ammonia, borates, and organic acids. The same buffer components also occur in fresh waters, but at such concentrations as to be singularly ineffective relative to the carbonates in the regulation of pH. Biochemical activities and heterogeneous equilibria provided by clays, minerals, and decomposition of igneous rocks are also important. Rigorous mathematical expressions from which quantitative evaluations of pertinent chemical systems can be made have been derived from mass law and electroneutrality considerations and have been applied to the carbonate system. Logical extension to other systems has been discussed.

DIAGENESIS AND WEATHERING

Precipitated silica may develop into clay minerals, silicify fossils, cement larger particles, form quartz, or form other silicate minerals. Outcrop silicates exposed to weathering may form other minerals; e.g., the iron may leach from a silicate mineral causing formation of a new mineral. Clay minerals may alter because of silicate reactions.

Most of the following references are about diagenesis. Additional research concerning both diagenesis and weathering is necessary to understand the silica cycle.

Selected References

21. Bogomolov, G. V., G. N. Plotnikova, and E. A. Titova. Silica in Subsurface Waters of Some Parts of the Russian Platform. Dokl. Akad. Nauk Beloruss. SSR, v. 8, No. 11, 1964, pp. 731-735.

Analyses of samples of subsurface waters from various parts of the Russian platform show that there is no relation between their amorphous silica content and their total mineral content, nor is there any relation with the mineral composition of country rocks and silica content of the waters.

The amount of H_2S dissolved in water does not influence the content of H_2SiO_3 in surface waters.

22. Dapples, E. C. The Behavior of Silica in Diagenesis. Paper in Silica in Sediments Symposium. Soc. Econ. Paleontologists and Mineralogists, Special Pub. 7, 1959, pp. 36-54.

Chemical reactions between detrital minerals, the incorporated biota and their tests, and interstitial fluids are considered to tend toward equilibria under three different stages of diagenesis of sediments. Such stages are initial or depositional, intermediate or early burial, and late burial or premetamorphic. Collectively, the effect upon quartzose sandstones is as follows: (1) During deposition, there is distinct pitting and rounding of quartz grains by solution, and instability of detrital chert; i.e., minor but persistent solution of silica. (2) Early burial is characterized by precipitation of quartz as overgrowths; i.e., minor but characteristic precipitation of quartz. (3) Late burial is characterized by addition of carbonate cement and as a replacement of quartz grains; or, where carbonate is absent, interpenetration of quartz grains increasing in degree with depth of burial or application of pressure as indicated by folding. Among subgraywacke sandstones, chert tends to be metastable during the early burial stage and reacts with clay to form authigenic clay minerals and micas. Deep burial is characterized by introduction of carbonates corroding quartz and replacing the clay matrix and authigenesis of mica from interstitial clay.

Occurrence of silica in Silurian carbonates with coral reef development shows interrelationships between carbonate minerals and chert which indicate chert is introduced during lithification of the reef flank sediments and precedes dolomitization.

Analyses of saline formation waters from Paleozoic carbonate strata buried to depths of several thousands of feet within the Illinois Basin provide data which suggest that solubility of silica is independent of pH below values of 8, and that temperature may be the important control of silica solubility.

23. Ireland, H. A. Introduction to Silica in Sediments. Paper in Silica in Sediments Symposium. Soc. Econ. Paleontologists and Mineralogists, Special Pub. 7, 1959, pp. 1-3.

Silica occurs as amorphous to crystalline form in many types of igneous, metamorphic, and sedimentary rocks, but in sediments and sedimentary rocks much of the silica is detrital material. The chief forms of silica are hydrous opal, cryptocrystalline chalcedony, and crystalline quartz.

The primary aim of this symposium on silica in sediments is chiefly toward the geochemical and organic aspects rather than the study of detrital particles of silica. However, clastic deposits of siliceous organisms, volcanic ash, and other clastics serving as sources of silica are of interest.

Sedimentary silica enters into the development of authigenic quartz and silicates, into clay minerals, and into other secondary compounds as a result of geochemical action. The precipitation of chert, silicification of fossils, formation of skeletal parts and coverings of organisms, cementation of particles, and the relation of silica to diagenesis are matters which warrant research and discussion.

Knowledge of the various aspects of silica in sediments is important economically in regard to mineral deposits, petroleum geology, and ground water. Regeneration of quartz particles, cementation by silica, and differential solution have a great effect on porosity and permeability of aquifers and petroleum reservoirs, thereby reducing or increasing petroleum or water accumulation.

24. Keller, W. D. The Bonding Energies of Some Silicate Minerals. Am. Miner., v. 39, 1954, pp. 783-793.

The bonding energies of some silicate minerals may be computed by adding the energies of the bonds between their constituent cations and oxygen, starting with the elements in the gaseous ionic state. Data from Huggins and Sun are used in the computations.

Bonding energies of micas, micalike materials, some common metamorphic minerals, and of minerals in the Bowen Reaction Series were compared, after the bonding energies were adjusted to a standard mineral cell containing 24 oxygens. Fair agreement, but not complete, between the order of bonding energy and that of mineral occurrence is observed.

It is concluded that the genesis of a mineral involves the energy balance present in its environment during formation, as well as the availability (concentration and activity) of its constituent elements, their ionic size, electronegativity, force fields, coordination, and other factors.

25. Keller, W. D. Argillation and Direct Bauxitization in Terms of Concentrations of Hydrogen and Metal Cations at Surface of Hydrolyzing Aluminum Silicates. Bull. Am. Assoc. Petrol. Geol., v. 42, No. 2, February 1958, pp. 233-245.

Some observations have shown that certain aluminum silicate rocks weather directly to bauxite, but other observations indicate that the same rock types weather elsewhere to kaolinite which may then undergo weathering to bauxite (bauxite refers herein to a rock composed dominantly of hydrated aluminum oxide). These contrasting differences in initial products of weathering are explained by relating their separate origins to differences in pH at the surfaces of the parent minerals while undergoing hydrolysis. The pH at a mineral surface during hydrolysis is taken from the abrasion pH of the mineral.

From data of Correns, both Al_2O_3 and SiO_2 are reported to be relatively soluble at pH above 10; at pH 7 to 9.5, Al_2O_3 is very sparingly soluble but silica is moderately soluble, thereby conducing toward direct bauxitization of an aluminum silicate; in the range of pH from about 7 to 4.5, the solubilities of both Al_2O_3 and SiO_2 are low, giving rise probably to clay minerals as the products of hydrolysis of a parent aluminum silicate. Profuse rainfall conduces toward complete solution of silica and monovalent and divalent metal cations, and therefore leads toward bauxitization of minerals having a high abrasion pH (alkaline); whereas, periodic and scanty rainfall, and also minerals having a relatively low abrasion pH, tend toward the production of clay minerals during weathering. The divergence between direct bauxitization and intermediary argillation is thereby reconciled.

26. Loughman, F. C. Some Considerations in the Weathering of the Silicate Minerals. J. Sedimentary Petrol., v. 32, No. 2, June 1962, pp. 284-290.

The weathering of the silicate minerals is considered a function of two variables, (1) the mobilities of the essential cations and (2) the mineral structure. It would appear that in the normal pH range of 4 to 10, the leaching potential is the most important factor influencing the mobilities of the cations though the oxidation-reduction potential considerably affects the solubility of iron. Parent mineral structures are instrumental in controlling the accessibility of the percolating waters to the bonding cations.

27. Mattson, S. The Laws of Soil Colloidal Behavior. 9. Amphoteric Reactions and Isoelectric Weathering. Soil Sci., v. 34, No. 3, 1932, pp. 209-240.

If an insoluble weak base as represented by $B(OH)_3$ reacts with a weak acid, as represented by H_2A , to form an insoluble compound, then we may have (a) $HA[B(OH)_2]_2$, (b) $HA = BOH$, (c) $(H_2A)_2 BOH$, or any intermediate combination.

These compounds contain acid and basic residues of varying strength and react amphotERICALLY. Where the acid residue is weak, as in (a), the isoelectric pH will be high and where the acid residue is strong, as in (c), the isoelectric point will be at a low pH. This relation between the composition and the isoelectric pH, which has previously been experimentally verified, has been applied to a study of the process of weathering. It is in general true that amphoteric compounds are least dispersible, least soluble, and least ionized, and are therefore most stable at their isoelectric point. Therefore, under conditions of heavy leaching, the tendency would be for the formation of an isoelectric soil complex.

The proportion of silicic acid isoelectrically precipitated by aluminum and iron increases as the pH decreases. Aluminum hydroxide, being a stronger base than ferric hydroxide, binds the greatest proportion of the acid at any given pH. In neutral or alkaline environment, the ferric oxide is the first of the amphoteric sesquioxides to be set free. Even in colder, more acid soils, red ferric oxide is always in evidence. The ratio of silica to strong bases in river waters and soil colloids increases geographically from north to south.

28. Sanders, J. E., and J. P. Swinchatt. Deep-Sea Origin of Radiolarian Cherts. Abs. in Bull. Geol. Soc. Am., v. 68, 1957, p. 1791.

Consideration of the literature describing radiolarian cherts and results of deep-sea-sediment investigations made since Davis' (1918) summary of the origin of the Franciscan cherts (California) in which the "deep-water" hypothesis was rejected convinces the writers that the "deep-water" hypothesis of radiolarian cherts is correct. Not all problems raised by these cherts are resolved by this interpretation, but all commonly cited objections to it--association with coarse clastic strata, presence of ripple marks in associated beds, alternation of chert and shale beds, and presence of plant remains--can now be shown to be ambiguous for environmental determination owing to turbidity-current transport of "shallow-water" material into oceanic depths.

If the "deep-water" interpretation is correct, great vertical movements of the crust have taken place where radiolarian cherts are now exposed. Identification of these cherts as ancient deep-sea sediments seems to answer the query as to the whereabouts in the geologic record of the counterparts of modern deep-sea trenches; they are in those geosynclines in which radiolarian cherts were deposited.

29. Weller, W. W., and K. K. Kelley. Low-Temperature Heat Capacities and Entropies at 298.15° K of Crystalline Silicates of Barium and Strontium. BuMines Rept. of Inv. 6556, 1964, 8 pp.

The heat capacities of four crystalline silicates of barium (BaSiO_3 , Ba_2SiO_4 , $\text{Ba}_2\text{Si}_3\text{O}_8$, and BaSi_2O_5) and two crystalline silicates of strontium (SrSiO_3 and Sr_2SiO_4) were measured over the temperature range from 51° to 298° K. The results were used to evaluate the entropies at 298.15° K. The entropy values were joined with known heats of formation to obtain the free energies of formation of the silicates with respect to their constituent oxides at 298.15° K.

30. Wilson, R. C. L. Silica Diagenesis in Upper Jurassic Limestones of Southern England. J. Sedimentary Petrol., v. 36, No. 4, December 1966, pp. 1036-1049.

Silica diagenetic fabrics occurring in the Portland and Corallian beds of southern England are described. On the basis of their morphology, five major fabric types are distinguished: mosaic quartz, chalcedonic overlays, spherulitic chalcedony, lutecite, and micro-crystalline granular quartz. Of these, the first three may be cementation fabrics, and all excepting chalcedonic overlays may exhibit replacement features.

The silica fabrics are dated according to their relation to carbonate diagenetic fabrics. Two major stages of silicification are demonstrated, the first being pre-calcite-cement fabrics, and the second post-calcite-cement fabrics; each was probably accompanied by calcitization of sponge spicules. The latter occur in sufficient quantities throughout the sediments to account for the silica fabrics. Lack of silicification in the Corallian beds, despite their high spicule content, is probably caused by calcite cements effectively reducing porosity early in their diagenetic history. This contrasts with the extensive development of cherts in the Portland beds, in which high porosities are maintained after deposition to the present day.

HYDROTHERMAL REACTIONS

Many of the hydrothermal reactions cited are closely related to diagenesis. The references are separated into two groups. The first group contains information about reactions occurring in nonsaline aqueous media. The two groups are not sharply differentiated; however, the aqueous media in the second group is more saline than the aqueous media in the first group.

Most of the research deals with synthesis of silicates and their hydrothermal chemistry. Considerable contemporary research is in progress in this area.

Selected References

A. In Nonsaline Media

31. Barrer, R. M. Factors Concerning the Growth of Crystalline Silicates. Disc. Faraday Soc., No. 5, 1949, pp. 326-337.

The principal synthetic methods in silicate mineral chemistry are referred to.

32. Barrer, R. M. Preparation of Synthetic Quartz. Nature, v. 157, No. 3996, June 1, 1946, p. 734.

A partial or complete crystallization of silicic acid gel was obtained by heating the gel with potassium carbonate or sodium carbonate solution for 3 days at 350°-390° C in an autoclave. Quartz was the only crystalline species present. Quartz was also obtained in admixture with crystals of other materials by hydrothermal crystallization of aluminosilicate gels. Mixtures of low silica content did not give any quartz. The formation of tridymite and cristabolite has been reported under similar hydrothermal conditions.

33. Barrer, R. M. Syntheses and Reactions of Mordenite. J. Chem. Soc., 1948, pp. 2158-2163.

Mordenite has been crystallized in good yield from aqueous suspensions of sodium aluminosilicate gels of compositions ranging from Na_2O , Al_2O_3 , 8.1 SiO_2 , nH_2O to Na_2O , Al_2O_3 , 12.3 SiO_2 , nH_2O , the best temperature range being 265°-295° C; pH is as important as composition or temperature in ensuring a yield, and the best results were for a range of pH between 8 and 10 in the cold mother-liquor after crystallization.

Simultaneously with mordenite, some analcite was obtained mainly at the silica-poor end of the composition range, and some quartz at the silica-rich end. Outside the best temperature range (265°-295° C) species other than these three were observed, and yields of mordenite decreased. In very alkaline solutions mordenite crystals were readily precipitated at first, but tended to redissolve and disproportionate if left too long in contact with the mother-liquor at these high temperatures.

Mordenite undergoes a ready base exchange, nitrates and chlorides giving at least partial cation replacements according to the series

This accords with the open molecular sieve character of the mineral, and the products when dehydrated were themselves good sorbents of gases.

It is pointed out that zeolites, such as mordenite, must be regarded statistically as defect structures, in which a possibly large number of new configurations introduced by base exchange give rise to a configurational entropy term. The occurrence or nonoccurrence of exchanges of the types $\text{K}^+ \rightleftharpoons \text{Na}^+$, $\text{Ca}^{++} \rightleftharpoons 2\text{Na}^+$ may be influenced by the size of this entropy term relative to the corresponding energy changes.

34. Barrer, R. M., and E. A. D. White. The Hydrothermal Chemistry of Silicates. Part 1. Synthetic Lithium Aluminosilicates. J. Chem. Soc., 1951, pp. 1267-1278.

Hydrothermal methods were used to investigate the crystallization of materials from $\text{Li}_2\text{O} - \text{SiO}_2 - \text{H}_2\text{O}$, $\text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$, and $\text{Li}_2\text{O} - \text{nSiO}_2 - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ gel systems, in which n varied from 1 to 10.

Materials were heated in bombs to temperatures to 150°-450° C. The pH of the resulting solutions was measured, and crystals formed were characterized by optical and X-ray studies. Lithium silicate and α -quartz were produced in the first systems; boehmite, γ -alumina, and lithium aluminate by the second system; and, in addition, α -petalite, α - and β -encryptite, α - and β -spodumene, and two other lithium aluminosilicates in the third system. The latter two materials showed the sorptive behavior of zeolites and underwent a variety of ion-exchange reactions involving Li^+ , Ag^+ , Na^+ , K^+ , Rb^+ , Tl^+ , NH_4^+ , Ca^{++} , and Ba^{++} . Upon ignition, β -encryptite and β -spodumene were formed.

35. Clark, R. H., and W. S. Fyfe. Ultrabasic Liquids. *Nature*, v. 191, 1961, pp. 158-159.

Hydrothermal treatment of serpentine of 500 to 1,000 atmospheres indicated that, at above 500° C, the serpentine was replaced by talc and forsterite and that, at higher temperatures, forsterite, enstatite, and minor chromite were dominant. Between 900° and 1,200° C, pyroxene and olivine were fine grained. Flowage occurred at 1,300°-1,400° C. After the samples had been quenched, feathery growths of olivine or pyroxene appeared. This behavior is discussed in relation to the flow of serpentine lava in a submarine environment.

36. De Kimpe, C., M. C. Gastuche, and G. W. Brindley. Ionic Coordination in Alumino-Silicic Gels in Relation to Clay-Mineral Formation. *Am. Miner.*, v. 46, 1961, pp. 1370-1381.

Gelled and crystalline Al and Mg silicates were synthesized at low temperatures and pressures. The main factors in the kind of crystals synthesized were salt concentration, pH, and ratio of Mg or Al content to silica content. Kaolinite, serpentine minerals, and mica were produced at low, intermediate, and higher pH's, respectively.

37. Flaschen, S. S., and E. F. Osborn. Studies of the System Iron Oxide-Silica-Water at Low Oxygen Partial Pressures. *Econ. Geol.*, v. 52, No. 8, December 1957, pp. 923-943.

In hydrothermal studies of iron oxide-silica-water mixtures at low partial pressures of oxygen, the ferrous silicates, fayalite, greenalite and minnesotaite have been synthesized and their stability relations investigated. Equilibrium relationships among phases in the system $\text{FeO-Fe}_3\text{O}_4\text{-SiO}_2\text{-H}_2\text{O}$ are discussed in relation to mineral assemblages of Lake Superior iron formation.

38. Gastuche, M. C., and C. De Kimpe. Synthesis of Kaolin Clays at Normal Temperature and Pressure Conditions. *Bull. Classe Sci. Acad. Royale Belgique*, v. 45, 1959, pp. 1087-1104.

The effect of NaCl concentration, Si source, Al source, pH of formation, and reactant concentration was determined on the synthesis of kaolinite and muscovite from solutions containing Al and Si ions during a reaction time of 2 months. Gels and a small amount of crystalline material were formed. The presence of NaCl favors flocculation of the gels. Where Al was replaced by Mg, a product similar to serpentine was produced.

39. Gillingham, T. E. The Solubility and Transfer of Silica and Other Non-Volatiles in Steam. *Econ. Geol.*, v. 43, No. 4, June-July 1948, pp. 241-272.

Recent experiments show that several non-volatile substances are appreciably soluble in supercritical steam at pressures above 200 kg/cm². Steam at 450° C and 304 kg/cm² dissolves 240 ppm of silica from gel. Higher pressures caused by rise in temperature increase solubility. Also, at constant temperature, solubility increases with rise in pressure.

By placing various oxides or carbonates in platinum crucibles near the top of a steel bomb and water and silica gel in the bottom, silica is transferred through steam at a rate that increases with pressure and is dependent upon the "reaction potential" between silica and the substances in the crucibles.

Kaliophilite, muscovite, pyrophyllite, wollastonite, serpentine, forsterite, brucite, and talc were synthesized. Wollastonite was formed by transfer of silica to Iceland spar. Silica and magnesium oxide formed serpentine and brucite when the temperature was below about 435° C and forsterite and brucite when the temperature was higher. At 522° C and about 650 kg/cm², talc and forsterite were obtained. In experiments involving temperatures above 450° C, the silica gel frequently altered to euhedral crystals of quartz. If this happened, transfer would be very much slower on account of a lowered reaction potential.

It may be concluded that steam at pressures above 300 kg/cm² is a powerful solvent of nonvolatiles such as silica. Pressure may be almost as important as temperature in the formation of mineral deposits by emanations.

40. Hatch, R. A. Phase Equilibrium in the System: $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 - \text{SiO}_2$. *Am. Miner.*, v. 28, Nos. 9 and 10, September-October 1943, pp. 471-496.

Liquidus and solidus temperatures for almost all of the 21 preparations along the line $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, from 85 to 22 percent silica, have been determined. Three component compounds in the system are β -spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, high-temperature form melts congruently at $1,423^\circ \text{C}$) and β -eucryptite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ melts with dissociation at $1,397^\circ \text{C}$). No compounds having the compositions of petalite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$) "lithium orthoclase" ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) are stable above the solidus. Petalite dissociates at 950°C or less.

This system includes five or six fields: (1) the silica field, (2) the field of β -spodumene silica solid solution, (3) the field of β -spodumene solid solution, (4) the field of β -eucryptite solid solution, (5) the γ -alumina field, and (6) the lithium aluminate field (?). Fields (1) and (2) appear to be binary; fields (3) and (4) are essentially binary at the liquidus but show ternary behavior 10° to 80° below the solidus, small amounts of mullite and/or α -alumina separating from the solid solution series; field (5) is ternary.

Attempts to synthesize α -spodumene (mineral) hydrothermally at pressures below 100 atmospheres and at temperatures of 400° to 550°C failed. In every case, β -spodumene crystallized from the spodumene glass.

41. Hemley, J. J. Some Mineralogical Equilibria in the System $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$. *Am. J. Sci.*, v. 257, April 1959, pp. 241-270.

An experimental investigation was made at elevated temperatures and pressures of the hydrolysis of KAlSi_3O_8 (K-feldspar) to $\text{KAl}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ (mica) + silica and of mica to $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite). Values of the equilibrium quotient, $M_{\text{KCl}}/M_{\text{HCl}}$, were determined at temperatures ranging from 200° to 550°C . The solution pressure for most of the runs was 15,000 psi, although determinations were made at both higher and lower pressures. The reactions are exothermic and the equilibria show a marked shift to higher acidities with increasing temperature. The equilibrium curves for the two reactions are essentially parallel. Above about 350°C , the assemblage mica-kaolinite changes to mica- $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ (pyrophyllite)- $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (boehmite), and at still higher temperatures mica-pyrophyllite-andalusite (Al_2SiO_5) is formed. At 400°C and 15,000 psi, the equilibrium quotient is $10^{2.7}$ for the assemblage K-feldspar-mica-silica, and $10^{1.3}$ for the assemblage mica-pyrophyllite-boehmite. The experimental equilibrium quotients probably do not differ from the thermodynamic equilibrium constants of the reactions by more than a factor of 5 up to temperatures of 350°C or higher.

The experimentation shows that the most important controls on the fields of stability of these several minerals are the K^+/H^+ activity ratio and the temperature. At a given temperature and with increasing K^+/H^+ ratio, the fields of kaolinite, mica, and K-feldspar are successively traversed. Similarly, at constant K^+/H^+ ratio with increasing temperature, the same sequence is observed. The free energy drive of hydrolysis decreases with increasing temperature. Thus, the alteration potential of hydrothermal solution would increase with decreasing temperature provided the rate of migration were sufficiently rapid in comparison with the rate of reaction with the wall rock. Experiments at solution pressures of 5,000 to 35,000 psi show that the effect of solution pressure on these equilibria is relatively small. An increase in pressure increases the extent of hydrolysis, whereas a decrease in pressure shifts the equilibria in the opposite direction.

The experimental results have particular application to hydrothermal alteration and the genetic interpretation of various alteration mineral patterns.

42. Hénin, S., and O. Robichet. New Results Concerning the Preparation of Argillaceous Minerals in the Laboratory; Synthesis of Autigorite. *Compt. rend.*, v. 238, 1954, pp. 2554-2556.

Autigorite was prepared by slowly adding dilute solutions of sodium silicate and aluminate to 2 liters of a solution containing 100 g NaCl, 10 g $MgCl_2$, and 2 g $CaCl_2$.

43. Hénin, S., and O. Robichet. Synthesis of Clay Minerals. *Clay Minerals Bull.*, v. 2, 1954, pp. 110-114.

Magnesium montmorillonite and possibly sepiolite were produced by slowly adding dilute solutions of silica and magnesia to a buffered boiling-water reservoir.

44. Hoyas de Castro, A., and M. Delgado. Effect of Thermal Treatment on the Serpentine of Barranco de San Juan. 21st Internat. Geol. Cong. Rept., Copenhagen, Denmark, 1960, pt. 24 (pub. 1961), pp. 64-72.

Dehydration curves to 1,300° C are given for samples of serpentine.

45. Koltermann, M. Magnesium Silicates at High Temperatures. *Naturwissenschaften*, v. 51, No. 12, 1964, p. 287.

In the presence of an oxidizing atmosphere, serpentine or sepiolite forms X-ray amorphous MgSiO_3 at 700°C . The conversion products of enstatite, protoenstatite, talc, bronzite, and clinoenstatite are also listed.

46. Luth, W. C. The System $\text{KAlSiO}_4\text{-Mg}_2\text{SiO}_4\text{-SiO}_2\text{-H}_2\text{O}$ from 500 to 3000 bars and 800 to 1200° and Its Petrologic Significance. Ph.D. Thesis, Pennsylvania State Univ.; University Microfilms, Ann Arbor, Mich., 1964, 159 pp.
47. Luth, W. C., and O. F. Tuttle. The Alkali Feldspar Solvus in the System $\text{Na}_2\text{O-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. *Am. Miner.*, v. 51, Nos. 9/10, September-October 1966, pp. 1359-1373.

Preliminary experiments in the system $\text{Na}_2\text{O-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ indicate that the nature of the alkali feldspar solvus is influenced by the $\text{Na}_2\text{O} + \text{K}_2\text{O}:\text{Al}_2\text{O}_3$ molar ratio in the bulk composition. The solvuses obtained by the crystallization of dehydrated gels in the presence of an aqueous vapor phase at 2 kilobars show significant differences which are dependent on the stoichiometry of the initial bulk composition. This feature may be a consequence of differences in thermal state in the various synthetic feldspars, or it may reflect a departure from stoichiometry. Analysis of unit cell dimensions suggests that the alkali feldspars crystallized in the presence of excess Al_2O_3 contain minor amounts of excess Al_2O_3 in crystalline solution. Unit cell dimensions of those alkali feldspars crystallized in the presence of excess $\text{Na}_2\text{O} + \text{K}_2\text{O}$ suggest that in this case a lower thermal state is obtained.

48. Merenkov, B. Ya. The Genesis of Chrysotile Asbestos. *Tr. Inst. Geol. Rudn. Mestorozhd., Petrogr., Mineralog. i Geokhim.* No. 22, 1958, pp. 3-138.

This article is a treatise on serpentine asbestos, covering chemical analyses, synthesis, chemical composition of asbestos-forming liquids, and the mechanism of its formation.

49. Morey, G. W., and E. Ingerson. The Pneumatolytic and Hydrothermal Alteration and Synthesis of Silicates. *Econ. Geol.*, v. 32, supp. to No. 5, August 1937, pp. 607-760.

This article contains a summary, including abstracts, of earlier literature, and a discussion of experimental work and theoretical principles.

50. Ni, L. P., and L. V. Bunchuk. Interactions in the System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaO}-\text{H}_2\text{O}$ Under the Conditions of Hydrochemical Processes and at Varying Ratios of $\text{CaO}:\text{SiO}_2$. Trudy Inst. Met. i Obogashch., Akad. Nauk Kaz. SSR, v. 9, 1964, pp. 56-62.

Analyses were made of both filtrates and precipitates from the hydrothermal reaction of sodium aluminate, Al_2O_3 , CaO , and SiO_2 gel at 280°C . Effects of varying the ratio of $\text{CaO}:\text{SiO}_2$ were studied.

51. Noguchi, K., and J. Nix. Geochemical Studies of Some Geysers in Yellowstone National Park. Proc. Japan Acad., v. 39, No. 6, 1963, pp. 370-375.

In the early and late stages of an eruption, when the water is from shallow zones, water is relatively high in SO_4 content and relatively low in Cl , SiO_2 , total solids, and alkalinity. During the peak of the eruption, when the water is from deeper zones, SO_4 content is relatively low, and Cl , SiO_2 , total solids, and alkalinity are relatively high.

52. Olsen, E. Equilibrium Calculations in the System Mg , Fe , Si , O , H , and Ni . Am. J. Sci., v. 261, 1963, pp. 943-956.

Calculations were made for the hydrothermal reactions of serpentine + brucite = forsterite + H_2O + $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ = talc + MgSiO_4 + H_2O .

53. Pistorius, C. W. F. T. Some Phase Relations in the System $\text{MgO}-\text{SiO}_2-\text{H}_2\text{O}$ to High Pressures and Temperatures. Neues Jahrb. Miner., Monatsh., No. 11, 1963, pp. 283-293.

Pressure-temperature phase diagrams are given for equilibria up to 30-60 kilobars of hydrothermal transformations of serpentine, brucite, forsterite, talc, enstatite, and quartz. Serpentine, when heated in the presence of water vapor, decomposes to forsterite, talc, and water according to the equation:

54. Roy, D. M., and R. Roy. Synthesis and Stability of Minerals in the System $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Am. Miner., v. 40, 1955, pp. 147-178.

Phase equilibria in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ were studied in order to obtain further information on the stability of metamorphic minerals and mineral assemblages. The equilibria are described in terms of composition triangles, of phases in equilibrium with H_2O .

Seventeen sets of triangles are given to describe changing equilibria with increasing temperature, at a constant water pressure of 10,000 psi. Syntheses of phases and equilibrium data are discussed, along with factors influencing the attainment of equilibrium.

At low temperatures, montmorillonite "solid solutions" cover a large field in the high-silica portion of the diagram, whereas mixtures high in magnesia yield aluminian serpentine, in combination with other phases. Alumina hydrates and kaolinite dominate the high-alumina portion of the diagram in this temperature range. Aluminian serpentine at higher temperatures gives way to clinochlore. Cordierite, the only anhydrous ternary phase encountered, is stable in equilibrium with H_2O above ca $500^{\circ}C$, and the stable joins, quartz-cordierite- H_2O and cordierite-spinel- H_2O , divide the quarternary system into two areas: that part dominated by the alumino-silicates, and the area involving magnesium silicates. In the alumina-silica side of the system pyrophyllite is the hydrate stable to the highest temperature, $575^{\circ}C$; but, in the magnesia-silica side, talc is stable to a much higher temperature, $780^{\circ}C$. Applications of the data obtained to geologic problems are discussed.

55. Roy, R., and E. F. Osborn. Some Simple Aids in the Hydrothermal Investigation of Mineral Systems. *Econ. Geol.*, v. 47, No. 7, November 1952, pp. 717-721.

Modifications of existing pressure equipment for hydrothermal studies are described. These include the use of a jack as a simple means of generating high pressures in standard vessels, the conversion of pressure vessels into rod mills for grinding at elevated temperatures and pressures, and changes in design of pressure vessels.

56. Roy, R., and E. F. Osborn. The System $Al_2O_3-SiO_2-H_2O$. *Am. Miner.*, v. 39, No. 11/12, November-December 1954, pp. 853-885.

A fundamental approach has been attempted in the study of the temperatures of formation and limits of stability of certain clay minerals and metamorphic rock assemblages. This has been done by studying the phase equilibrium relationships in the system $Al_2O_3-SiO_2-H_2O$ under conditions of independently controlled temperature and water-vapor pressure. The data from a large number of runs are presented in a series of compatibility triangles for various temperatures and pressures. The equilibrium decomposition temperature of the kaolinite minerals has been placed at $405^{\circ}C$ (at 10,000 psi water pressure) and that of pyrophyllite at $575^{\circ}C$. Two new clay-phases exist in the

system and are described in detail, one a pure Al-Si montmorillonite and the other herein named hydralsite, one of the decomposition products of kaolinite. The application of the results to geological and ceramic problems is discussed.

57. Sand, L. B., R. Roy, and E. F. Osborn. Stability Relations of Some Minerals in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ System. *Econ. Geol.*, v. 52, No. 2, March-April 1957, pp. 169-179.

Equilibrium relationships among mineral phases in the low soda part of the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ are presented. Assemblages of three crystalline phases in equilibrium with an aqueous phase at elevated water pressure (5,000-30,000 psi) are arranged in order of increasing temperature of stability, with relationships shown diagrammatically by a series of phase triangles. Upper temperature limits of stability at high water pressures are given for analcite, paragonite, hydroxy-sodalite, hydroxy-cancrinite, Na-montmorillonite, and a nepheline hydrate phase.

58. Stringham, B. Fields of Formation of Some Common Hydrothermal-Alteration Minerals. *Econ. Geol.*, v. 47, No. 6, September-October 1952, pp. 661-664.

The problems of identification of the fine-grained hydrothermal alteration minerals are fairly well advanced. The fields of formation at which these minerals were formed are not so well known. Some common hydrothermal minerals have been arranged on a chart, the abscissa of which represents the pH of the depositing solutions, while the ordinate represents temperature. The chart is presented with a multiple purpose--i.e., to present in readily usable form the known information regarding the field of formation of minerals; to serve as a stimulus to students to attack the hydrothermal problem from a laboratory viewpoint, and to bring out further information from individuals who may have better data. It is expected that the chart will change from time to time with the accumulation of new information.

59. Taylor, H. F. W. Hydrothermal Reactions Involving Thallium. *J. Chem. Soc.*, 1949, pp. 1253-1256.

Mixtures of thallos aluminate, silicate, and aluminosilicate compositions have been subjected to hydrothermal treatment at temperatures of 200°-350° C. Analytical, optical, and X-ray powder examinations of the insoluble products have shown that several crystalline species can be obtained in a reproducible manner. Analyses of one

species approximated to TlAlSiO_4 , analogous to kaliophilite and kalsilite (KAlSiO_4), but the X-ray powder spacings differed considerably from those of either of the potassium minerals. α -Cristobalite and α -quartz were obtained from the silica-rich mixtures, but only in the absence of alumina. A species $\text{TlAlSi}_2\text{O}_6$ obtained in good yield from mixtures of approximately its own composition readily underwent base exchange and showed a close structural similarity to leucite (KAlSi_2O_6) or analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), into which it could readily be converted. Thus univalent thallium can at least to a limited extent form aluminosilicates in which its role resembles closely that of sodium or potassium.

60. Tuttle, O. F., and N. L. Bowen. Origin of Granite in the Light of Experimental Studies in the System $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 - SiO_2 - H_2O . Geol. Soc. Am., Memoir 74, Nov. 21, 1958, 153 pp.

This paper deals with the experimental determinations of phase-equilibrium relations in the system $\text{NaAlSi}_3\text{O}_8$ (albite)- KAlSi_3O_8 (orthoclase)- SiO_2 - H_2O and with the application of these results to some petrologic problems.

The laboratory experiments can be divided into two categories: (1) study of the liquidus, solidus, and subsolidus phase relations in synthetic mixtures, and (2) study of natural minerals and rocks. Phase relations in the binary systems SiO_2 - H_2O , $\text{NaAlSi}_3\text{O}_8$ - H_2O , KAlSi_3O_8 - H_2O , the ternary systems $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 - H_2O , $\text{NaAlSi}_3\text{O}_8$ - SiO_2 - H_2O , KAlSi_3O_8 - SiO_2 - H_2O , and the quaternary system $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 - SiO_2 - H_2O were investigated with the aid of synthetic mixtures. Analyzed natural feldspars were used for subsolidus studies in the system $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 , and the beginning of melting temperatures of natural granites were studied and compared with synthetic granites.

Phase-equilibrium relations in the system SiO_2 - H_2O were considered in detail because the relations in this system are representative of those expected in all systems involving a rock-forming silicate and water. There are at least five invariant points in the binary system of which three involve liquid carrying 90 percent silica. The effect of pressure on the high quartz-tridymite inversion was investigated; 1000 kg/cm² pressure raised the inversion temperature approximately 180° C to 1,050° C. Alkali feldspars form a complete series of solid solutions above 660° C, but unmixed when held at lower temperatures.

61. Upite, A., Z. A. Konstant, and A. Vaivads. Hydrous Magnesium Silicates. 3. Synthesis of Magnesium Hydrosilicates From Magnesium Hydroxide Dehydrated at 400° and Silicic Acid. *Latvijas PSR Zinatnu Akad. Vestis, Kimijas Ser.*, No. 6, 1963, pp. 629-635.

Mixtures of SiO_2 , MgO , and H_2O were heated at 174.5° at pressures of less than 8 atm. At $\text{MgO}:\text{SiO}$ ratios of 4:1 and 2:1, serpentine was formed; at ratios of 1:4 and 1:1, sepiolite was formed.

62. Wendlandt, H. G., and O. Glemser. Reaction of Oxides with Water at High Pressures and Temperatures. *Angew. Chem.*, v. 75, No. 20, 1963, pp. 949-957; *Internat. Ed.*, v. 3, No. 1, January 1964, pp. 47-54.

The reactions of the oxides SiO_2 , MoO_3 , and WO_3 with steam at temperatures between 400 and 700° C and pressures of 5 to 500 atm were studied by means of the transfer method. The results were evaluated by a new method. In the system $\text{SiO}_2/\text{H}_2\text{O}$, the formation of gaseous $\text{Si}(\text{OH})_4$, $\text{Si}_2\text{O}(\text{OH})_6$, and $[\text{SiO}(\text{OH})_2]_x$ was found to occur in three different water-density ranges. In the systems $\text{MoO}_3/\text{H}_2\text{O}$ and $\text{WO}_3/\text{H}_2\text{O}$, the gaseous compounds $\text{MoO}_2(\text{OH})_2$ and $\text{WO}_2(\text{OH})_2$, which were already known, exist up to densities of approximately 0.05 g/cm³. At higher densities, at which the supercritical phase begins to show the properties of a liquid to an ever-increasing extent, isopolymolybdic or isopolytungstic acids appear.

63. White, D. E., W. W. Brannock, and K. J. Murata. Silica in Hot-Spring Waters. *Geochim. et Cosmochim. Acta*, v. 10, No. 1/2, 1956, pp. 27-59.

The silica in hot-spring waters and in a few cold waters was studied by means of the colorimetric ammonium-molybdate method of analysis. Murata found in 1947 that only a part of the total silica in aged samples of high-silica waters was determinable by the colorimetric method. Weitz, Franck, and Schuchard later showed that ammonium molybdate reacts readily with the monomeric form of silica (probably H_4SiO_4) but very slowly with polymeric silica. If the colorimetric measurement is completed in 2 or 3 minutes, only the monomer is determined.

Nearly all silica of hot springs is in the monomeric form. Solubility equilibrium exists between dissolved (monomeric) and amorphous silica. For the hot springs that were studied, the solubility is about 315 ppm at 90° C and 110 ppm at 25° C, which is very similar to Krauskopf's experimental data.

Monomeric silica polymerizes so slowly to colloidal silica that many waters are supersaturated with respect to amorphous silica. The rate of polymerization is influenced by pH, temperature, degree of supersaturation, presence of previously formed colloidal and gelatinous silica, and contact with opal and other substances. Supersaturated acid waters and alkaline waters with less than 100% supersaturation tend to remain supersaturated almost indefinitely, with little or no change. Precipitation of colloidal silica is favoured by high temperature and contact with opal.

Many connate and other ground waters, including some thermal springs, are much below saturation with respect to amorphous silica, probably because low-solubility quartz and chalcedony have been precipitating.

Quartz is favoured by relatively high temperature, slow rate of precipitation, and low degree of supersaturation, and is believed to form by deposition of monomeric molecules. Chalcedony is probably deposited when the degree of supersaturation is moderately high and the rate of deposition is relatively fast. The ranges of temperature over which quartz and chalcedony deposit no doubt overlap, but, if other factors are equal, quartz is favoured by high temperature.

Opal is favoured by relatively low temperature and rapid rate of precipitation. Although opal has probably been deposited at temperatures as high as 140° C, it is unstable and is slowly converted to chalcedony or quartz. Water that is saturated with respect to opal is highly supersaturated with respect to quartz. Opal is probably formed from monomeric or, more probably, the smaller polymeric molecules of silica, retaining some of their water content. Evidence is lacking for the direct conversion of gelatinous silica to opal. Some differences in solubility probably exist between amorphous opal and opal that shows X-ray patterns like that of cristobalite.

The suggestion is made that clay minerals form by combination of monomeric silica and a comparable form of monomeric alumina, which must have very low solubility in waters within the pH range of 5 to 9. Because of the abundance and relatively high solubility of silica, the proposed reaction, dissolved alumina + dissolved silica $\rightleftharpoons$ clay, is ordinarily displaced strongly to the right in hydrothermal alteration and in ordinary soil formation. With removal of free silica, aided by tropical rainfall and temperatures,

the reaction may be displaced to the left by dissolution and removal of silica from the system. Alumina, because of its very low solubility, remains as bauxite.

64. Wyart, J. Hydrothermal Synthesis of Minerals. Disc. Faraday Soc., No. 5, 1949, pp. 323-324.

Heating of SiO_2 powder and aqueous KOH in an autoclave at temperatures above the critical temperature of water results in the crystallization of SiO_2 . The $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{Na}_x\text{K}_{1-x}\text{AlSiO}_4$ systems are also studied.

Selected References

B. In Saline Media

65. Akahane, M., and H. Yano. Reactions of Aqueous SiO_2 -NaOH- CaCl_2 Systems at 200°C . Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sec.), v. 62, 1959, pp. 1357-1361.

Aqueous SiO_2 -NaOH- CaCl_2 solutions were reacted in an autoclave at 200°C in order to gain an insight into the mechanisms of Ca-silicate boiler scale formation. SiO_2 concentration in the final solution was lowest when equivalent amounts of NaOH and CaCl_2 were used and rose when the amount of NaOH was increased.

66. Barrer, R. M., and E. A. D. White. The Hydrothermal Chemistry of Silicates. Part 2. Synthetic Crystalline Sodium Aluminosilicates. J. Chem. Soc., 1952, pp. 1561-1571.

Crystal growth has been investigated in the hydrothermal treatment of gels composed of Na_2O , Al_2O_3 , $n\text{SiO}_2$ ($n = 1$ to 12), $n\text{H}_2\text{O}$, with or without the addition of sodium, chloride, sulfate, carbonate, or hydroxide. The effects of temperatures ranging from 150° to 450°C , of pH, and of composition were studied. Products were examined by optical and X-ray studies.

Among the products were nosean and sodalite (feldspathoids) which were formed when sodium sulfate and sodium chloride were present, respectively; albite (a feldspar) and analcite (a zeolite) from high-silica mixtures; paragonite (a mica) from low-silica gels; analcite, which dominated most of the regions; and also mordenite (a zeolite), cancrinite, nepheline (feldspathoids), quartz, and sodium silicate. A slight excess only of sodium hydroxide enhanced the ease

of crystallization in almost all cases. Relatively large crystals were often produced. In the presence of large molar excess of sodium hydroxide above 300° C, several new species appeared. Cancrinite, sodalite, and nosean underwent ion exchange with silver nitrate solutions and irreversibly sorbed dry HCl gas.

67. Dittmann, J. Experiments on the Synthetic Metasomatism of Magnesium Silicates. *Hamburger Beitr. Angew. Mineral., Kristallphys. und. Petrogenese*, v. 2, 1959, pp. 86-98.

MgCl₂ and MgCO₃ solutions at 250° C have little effect on olivine, but MgSO₄ solutions cause decomposition of the mineral to colloidal SiO₂, brucite, and Fe oxide hydrates. Dolomite plus silica produced serpentine plus calcite at temperatures below 375° C and, in addition, wollastonite at a temperature of 400° C.

68. Gruner, J. W. The Hydrothermal Alteration of Feldspars in Acid Solutions Between 300° and 400° C. *Econ. Geol.*, v. 39, No. 8, December 1944, pp. 578-589.

About 30 experiments, largely with feldspars, were made in HCl solutions at 300° to 400° C (one at 525° C). The concentrations of K and Al were varied to some extent. It was found that kaolinite forms only below 350° ± 10° C and muscovite above this temperature to as high as 525° C. Pyrophyllite may form over the whole range from 300° to 525° C though it may be only metastable below 350° C. K feldspars are metastable (probably also Na feldspars) at 400° C, provided the concentrations of the corresponding alkalis are high. Some of these reactions take place at such low pressures that the presence of a liquid phase in the bombs is precluded. The writer has attempted to explain some of the reactions.

69. Hemley, J. J. Hydrolysis of K-Feldspar and Mica at Elevated Temperatures and Pressures. *J. Phys. Chem.*, v. 63, 1959, p. 320.

The hydrolysis equilibria of KCl-HCl solutions of K-feldspar and K-mica were studied at temperatures of 200°-500° C and at solution pressures of 5,000 to 35,000 psi, using sealed platinum tubes. Equilibrium was approached from both directions. Above about 350° C, the thermal instability of kaolinite resulted in a change to a mica-pyrophyllite-boemite assemblage. The effect of solution temperature was shown to be small as compared to the effect of temperature and the K⁺/H⁺ ratio. The equilibria shifted to higher acidities with increasing temperatures. The standard free energy of some of the reactions was determined.

70. O'Neill, T. F. The Hydrothermal Alteration of Feldspars at 250° C. to 400° C. Econ. Geol., v. 43, No. 3, May 1948, pp. 167-180.

About 40 experiments with feldspars were made in K_2S solutions and in basic, neutral, and acidic concentrated solutions of NaCl or KCl at 250° to 400° C. Alumina or silica was added in some experiments. It was found that, in the presence of excess K ions, potash and soda feldspars alter to kaliophilite in solutions more basic than about 0.10 M K_2S and 0.08 N KOH. In less basic solutions and in solutions as acidic as 0.001 N, potash feldspar alters to soda feldspar in the presence of an excess of Na ions. The reaction can be reversed in the presence of an excess of K ions. For a short range of concentrations more acidic than 0.001 N, soda feldspar is stable for the time of the experiments, but in 0.020 N HCl soda feldspar alters to pyrophyllite. In the presence of alumina and excess K ions, soda feldspar alters to muscovite in solutions as basic as 0.010 N. In the presence of silica, substitution of Na in labradorite was noticeable in 0.050 N NaOH and nearly complete in 0.150 N NaOH. In less basic and in acidic solutions, no Na substitution was obtained. The writer has attempted to explain some of the reactions.

71. Schloemer, I. H. Hydrothermal, Synthetic, Simultaneous Crystallization of Orthoclase and Quartz. Radex Rundschau, 1962, pp. 133-156.

The system $KAlSi_3O_8-SiO_2-H_2O$ was studied at high temperatures and pressures. New data for the solubility of orthoclase was obtained. A 1% solution of KF doubled solubility of feldspar.

PRECIPITATION REACTIONS

Many silicate precipitation reactions occur. Precipitates from boiler solutions containing optimum quantities of silica and magnesium may form serpentine. Kaolinite may form in similar environments when aluminum is present. Silicates readily precipitate when the pH is below 6.

Solutions containing controlled amounts of aluminum are used to cause precipitation of silicates. Alumina depresses the solubility of quartz.

Several of the references cited in this section are concerned with diagenesis. Some are solubility related studies.

Selected References

72. Akahane, M., and H. Yano. Silicic Acid Solutions. 2. SiO_2 -NaOH- MgCl_2 Aqueous Solutions. Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sec.), v. 62, 1959, pp. 366-369.

Precipitates from the reaction at 20° and 100° C of aqueous solutions of MgCl_2 with alkaline solutions of silicic acid were studied, and a relationship between solution and precipitation determined. A solution with a low Na/Si ratio has an initial talc-type structure, and one with a high Na/Si has an antigolite type.

73. Aver'yanova, L. N. Use of X-Ray Phase Analysis To Study Boiler Deposits. Tr. Novocherk. Politekh. Inst., v. 25, 1955, pp. 164-169; Abs. in Ref. Zh., Fiz., 1956, Abs. 3858.

The powder X-ray method was used to study the phase composition of locomotive boiler scale and residues. The water supply consisted of a mixture of alkaline artesian water (75%) and river water. Each of the X-ray diagrams of the scale samples had lines which coincided with the characteristic lines found in powder diagrams of calcite and serpentine. The powder diagram of the boiler residue was that of pure calcite. The X-ray data were verified by means of thermographic analysis of the samples. It was established that Mg hydrosilicate, $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, which crystallizes in the form of serpentine, is present in the silicate scale from the heat-liberating parts of the boiler surface.

74. Bassett, H. Silicification of Rocks by Surface Waters. Am. J. Sci., v. 252, December 1954, pp. 733-735.

Weathering of basic rocks in Tanganyika leads to the formation of siliceous alkaline solutions which, traveling downhill, soak into any porous material in their path, including weathered rock of the same nature as that from which they have been derived. Silica is slowly deposited, silicifying rocks and minerals of many kinds. Jaspers result from silicification of the claylike insoluble residues of rock weathering. Silica still left in solution after these processes is carried into mbugas, lakes, and rivers and is there deposited along with calcium and magnesium carbonates.

75. Bien, G. S., D. E. Contois, and W. H. Thomas. The Removal of Soluble Silica From Fresh Water Entering the Sea. Geochim. et Cosmochim. Acta, v. 14, 1958, pp. 35-54; paper in Silica in Sediments Symposium, Soc. Econ. Paleontologists and Mineralogists, Special Pub. 7, 1959, pp. 20-35.

Determinations of soluble silica and chlorosity of water samples collected in and around the east Mississippi Delta showed that most of the soluble silica was removed from the river water by some process other than dilution with sea water. While biological uptake by diatoms can account for part of this removal, it is more likely that a major portion is removed by inorganic precipitation.

Laboratory experiments with river water and sea water showed that both suspended matter from the river water and electrolytes in the sea water are necessary for maximum inorganic precipitation. It is concluded that this process is an adsorption of soluble silica on suspended matter as it comes in contact with electrolytes, rather than a simple formation of salts with electrolytes. The inorganic removal can increase the weight of sediment in the water that may be expected to reach the bottom by a maximum of 4.5 percent.

76. Burke, O. W., Jr., and C. B. Jackson. Addition of Sea Water During Precipitation of Silica Pigment. U.S. Pat. 3,202,525, Aug. 24, 1965.

A siliceous material to be used as a rubber reinforcer is obtained by acidulating an aqueous solution of Na silicate at 20°-150° C with a mineral acid or CO₂ in the presence of sea water. The amount of sea water can vary from 0.5-15 liters/mole of alkalinity, calculated as Na₂O, of the Na silicate.

77. Dement'ev, B. G., and Y. V. Zenkevich. Deposition of Sodium Chloride and Silica in Turbine Indicators. Elektr. St., v. 34, No. 7, 1963, pp. 24-27.

NaCl increased the deposition of SiO₂. SiO₂ did not affect the deposition of NaCl.

78. Durov, S. A., and N. F. Posnikov. Silicate Incrustations Containing Serpentine. Tr. Novocherk. Politekhn. Inst., v. 121, 1961, pp. 39-43.

A slimy incrustation containing up to 60% serpentine is formed as the result of reaction between H₂SiO₃ and Mg(OH)₂ in boiler water. Maintaining lower alkalinity and increasing upper blowdowns help decrease the deposition of serpentine. Acid treatment and chipping are used to remove the coating.

79. Filatov, K. V. Formation of Chemical Composition of Ground Waters in the Middle Amur Area and Separation of the Silicate Waters in Classification of Natural Waters. Byul. Mosk. Obshchestva Ispytatelei Prirody, Otd. Geol., v. 39, No. 1, 1964, pp. 147-163.

Conditions in the Middle Amur area are favorable for the formation of acidic silicate ground waters. During migration to lower levels, when the waters become enriched with Cl^- , $\text{SO}_4^{=}$, and alkaline earth cations, the precipitation of SiO_2 and $\text{Al}(\text{OH})_3$ results in a conversion to alkaline $\text{HCO}_3\text{-Na}$ waters. During further movement $\text{HCO}_3\text{-Ca}$ waters are formed by carbonatization of Ca silicate and precipitation of SiO_2 hydrogel. It is believed that the classification of ground waters, which conventionally ignores the existence of silicate waters, should include silicate waters and include the data on the amount of dissolved SiO_2 .

80. Frankel, J. J., and L. E. Kent. Grahamstown Surface Quartzites (Silcretes). Trans. Geol. Soc. South Africa, v. 40, 1937, pp. 1-42.

It is postulated that during the formation of the Grahamstown peneplain, which was very near the sea, the subsoils of the residual deposits on the main peneplain became silicified by the upward migration of acidic colloidal solutions of silica derived by the quiescent leaching of the underlying rocks. The coagulation of this silica in the subsoils was doubtless aided by the presence in the soil of downward migrating solutions rich in sodium chloride, which was transported by the wind from the nearby sea.

The result of this silicification was the formation of a layer of silcrete, resting on residual clays where it overlies argillaceous formations, or directly on sandstones and quartzites in the case of the arenaceous. The process of formation of these silcretes in the subsoil was interrupted on several occasions. During these "inter-silicification" periods, the first formed silcretes often broke up by weathering, and when silicification again commenced, the resulting product was in part a "silcrete conglomerate." These alternating periods of silicification and nonsilicification are probably to be ascribed to climatic variations--it has been shown that a seasonal fluctuating water table is essential for the formation of the silcretes; if the climate became torrid (in which case the water table would sink below the subsoils) or too moist and uniform (when the water table would not fluctuate), silcrete formation would end.

81. Gastuche, M. C., and J. Uytterhoeven. Correlations of the Surface Properties of Silica and Its Behavior in Natural Media. Silicates Ind., v. 26, 1961, pp. 341-351.

Mixed gels of SiO_2 with Fe_2O_3 and Al_2O_3 are discussed from the viewpoint of structure and acidity degree. The precipitation of serpentine and kaolinite from SiO_2 - MgO - H_2O and SiO_2 - Al_2O_3 - H_2O systems was observed to be a function of pH and time. The role of SiO_2 migration in soil formation and soil dissolution is important.

82. Goto, K. Precipitation of Silica in the Presence of Aluminum. Bull. Chem. Soc. Japan, v. 29, No. 6, August 1956, pp. 740-741.

The addition of acidic solutions of AlCl_3 or of $\text{Al}_2(\text{SO}_4)_3$ to solutions of colloidal silica and to solutions of molecularly dispersed silica, followed by an adjustment with NaOH to a pH of 4 to 11, resulted in the precipitation of silica within certain pH limits and silica to Al ratios. The optimum pH values for the precipitation of colloidal and molecularly dispersed silica were 4.5 and 9, respectively. One milligram of aluminum precipitates as much as 40 mg of colloidal silica--a much smaller amount of aluminum than is required to precipitate molecularly dispersed silica.

83. Gray, J. A. Boiler Water Treatment: A Formula for the Control of Sludge and Scale in Internal (Carbonate) Treatment. J. Inst. Fuel, v. 30, 1957, pp. 577-591.

A survey has demonstrated that sludge and scale formation in low-pressure boilers can be controlled successfully by (1) restricting the carbonate alkalinity in the boiler to between 200 and 300 ppm (expressed as CaCO_3), and by (2) keeping the Mg hardness of the feed above a certain minimum level, as expressed in the formula $X_F = (100/\text{CaH}) [(\text{MgH}/3) - \text{SiO}_2]$, where SiO_2 is the silica content, and CaH and MgH represent the Ca and Mg hardness, respectively (expressed as CaCO_3). X_F is a dimensionless quantity and should be greater than 7 for satisfactory scale and sludge control. The formula was found to apply to all types of low-pressure boilers and raw water supply.

84. Grimm, W. D. Precipitation of Silica in Sediments Affected by Salines. Z. Deut. Geol. Ges., v. 114, No. 3, 1962 (pub. 1964), pp. 590-619.

It is known that the precipitation of SiO_2 is related to the presence of electrolytes in solution. One hundred samples of authigenic silica were found to be related to the presence of salines during diagenesis. Na and K salts usually cause the precipitation to occur in country rock adjacent to saline rock, whereas, with gypsum and anhydrite, the precipitation occurs in the saline rock itself.

85. Harder, H. Precipitation of Silicic Acid. *Geochim. et Cosmochim. Acta*, v. 29, No. 5, May 1965, pp. 429-442.

The low silica content of natural waters can be ascribed to inorganic precipitation of silica or to fixation and sedimentation of silica by organisms. In recent publications on the solubility of silica, inorganic precipitation of silica is considered unlikely.

Results of experiments show, however, that X-ray amorphous hydroxides of aluminum, iron, manganese, or magnesium can be used to remove silica quantitatively from very diluted, undersaturated solutions (3 mg SiO_2 /liter H_2O). Hydroxide-silicate precipitates are formed which contain up to 80% SiO_2 (calculated H_2O -free). The adsorbed quantities of silica depend on temperature (at low temperatures the content of SiO_2 in hydroxides is higher), on concentration of Al/Si in the solution and on the physical condition of crystallization (amorphous hydroxides adsorb more than crystalline ones). The concentrations selected for the experiments (0.3 mg Al_2O_3 /liter H_2O and 3 mg SiO_2 /liter H_2O) indicate that inorganic precipitates of silica can be of very considerable importance under natural conditions. There is no significant difference in the SiO_2 content of precipitates from fresh water and from sea water. Diagenesis can lead to the formation of various clay minerals and fine-grained quartz from the X-ray amorphous hydroxide-silica precipitates. For the content of SiO_2 in water, the adsorption of silica by hydroxides is decisive.

86. Hart, J. S. (assigned to Phillips Petroleum Co.). Removal of Silica From Uranium Leach Solutions. U.S. Pat. 3,105,734, Oct. 1, 1963.

The SiO_2 content of carbonate leach solutions is greatly reduced by treating the solutions with an Al oxide, hydrate, or soluble inorganic salt at 25°-100° C for a length of time required to precipitate an Al-Si compound.

87. Heitmann, H. G. Solubility of Silicic Acid in Water and Steam and Its Effect on Silica Deposits in Turbines. *Chemiker Zeitung*, v. 88, No. 22, 1964, pp. 891-893.

The solubility of silicic acid and of quartz in water and steam was determined at 50°-650° C and 0.3-300 kg/sq cm pressure. Deposits of silicic acid in steam turbines are substantially amorphous, with only small amounts of crystalline quartz. Silicates can be deposited in the presence of metallic oxides. Turbine deposits can be largely avoided with feedwater of the following compositions: electrical conductivity at 20° C (after cation exchange and CO_2 removal) < 0.1

$\mu\text{mho/cm}$; $\text{SiO}_2 < 0.01 \text{ mg/kg}$; total Fe < 0.005 ; other heavy metals < 0.001 ; and Na and K $< 0.01 \text{ mg/kg}$. The entire steam system, other than the turbine and condenser, should be cleaned with acid prior to using.

88. Hinz, W., and P. O. Kunth. The Precipitates of Magnesium Salt and Water Glass Solutions. Silikat Tech., v. 8, 1957, pp. 148-156.

The precipitate first formed is merely a coagulant produced by adsorption. Prolonged aging at low temperatures or a short-term treatment at 100°C causes a definite chemical reaction. The effect of varying the ratio of SiO_2 to MgO on the completeness of precipitation of the two reactants is discussed.

89. Kohle, H. Feed-Water Problems in Boilers of Low- and Medium-Pressure Stages. Vom Wasser, v. 29, 1962, pp. 218-241.

A diagram for the calculation of total salt content of boiler water from the total hardness content is given. SiO_2 can be removed by Mg precipitation, ion exchange, or by more radical methods.

90. Kot, A. A. The Quality of the Steam and the Water Regime in Cylindrical Boilers at High Pressures. Vnutrikotlovye Fiz.-Khim. Protssessy, Akad. Nauk SSSR, Energ. Inst., 1957, pp. 143-178.

In the subcritical region, the salt content of the steam increases slightly with increase of salt content of the feed. The amount of entrained silica in various parts of the boiler is dependent upon the ratio $\text{Na}_2\text{O}(\text{NaOH})$ to SiO_2 --increasing if the ratio drops below 1.0, decreasing if the ratio rises to 8-10, but still causing turbine vane deposits. At higher ratios, soluble deposits are formed. Removal of SiO_2 in a special separator rather than operating at high ratios is recommended. Turbine blade deposits do not form if the silica content of the saturated steam is held down to 0.010-0.015 mg $\text{SiO}_3^{--}/\text{kg}$.

91. Kuhnert, W. A. Removing Dissolved Silica From Alkaline Brines. U.S. Pat. 1,992,532, Feb. 26, 1935.

A brine is mixed with a hydrated and at least partially carbonated magnesia in an amount slightly less than that required to combine with all the dissolved silica to form Mg silicate. After a period of time, a crystalline precipitate of Mg silicate forms.

92. Lovering, T. S. The Leaching of Iron Protores: Solution and Precipitation of Silica in Cold Waters. *Econ. Geol.*, v. 18, No. 6, September 1923, pp. 523-540.

This paper presents the results of an investigation of the solvent action of various cold dilute solutions on silica, and the precipitation of silica from these solutions. Experiments indicate that acid sulfate waters act rapidly on silicates, but do not appreciably affect quartz, jasper, taconite, opal, or chalcedony, unless phosphates or fluorides are present. Alkalies attack all the minerals and rocks tested, though quartz, jasper, taconite, and the silicates suffered much less than opal and chalcedony. The best solvent of quartz, jasper, and taconite was found to be a solution of magnesium bicarbonate. Waters containing bicarbonates of calcium and magnesium attacked all the minerals and rocks that were tried, and to about the same degree.

For the formation of any iron ore from its protore, the silica dissolved must remain in a state of solution. Experiments have previously been reported which indicate that solutions of bicarbonates or of the various electrolytes contained in sea water are common precipitants of silica in nature. The experiments described in this paper seem to show that these reagents generally precipitate silica only from solutions which are much more concentrated than is usual in nature, and that even with concentrated solutions, complete precipitation is extremely rare. Much of the silica which is precipitated as secondary quartz or chalcedony before being finally removed from a protore probably comes out of solution when acid waters rich in silica are made alkaline in the presence of electrolytes.

93. Moore, E. S., and J. E. Maynard. Solution, Transportation, and Precipitation of Iron and Silica. *Econ. Geol.*, v. 24, 1929, pp. 365-402.

A laboratory study was made of the agents which dissolve Fe_2O_3 and SiO_2 , of the nature of the chemical compounds that prevail during transportation in natural waters, and of the agents that bring about precipitation to form characteristic striata.

94. Okamoto, G., T. Okura, and K. Goto. Properties of Silica in Water. *Geochim. et Cosmochim. Acta*, v. 12, No. 1/2, 1957, pp. 123-132.

In view of the discordant theories for the mechanism of sedimentation of silica in natural waters, chemical properties of silica have been studied further. The solubility of amorphous silica has been measured over a wide range of pH and temperature. The study

on the depolymerization of colloidal silica indicated that sea water is not saturated with respect to molecularly dispersed silica. The presence of a small amount of aluminum greatly influences the state of silica in water. Thus, colloidal silica can be precipitated even by a trace amount of aluminum, while a larger amount of the latter is required for the precipitation of molecularly dispersed silica. The optimum pH for the precipitation of colloidal silica is about 4.5 in contrast to that of about 8 for molecularly dispersed silica.

95. Rao, A. V. R., D. S. Datar, and S. H. Zaheer. Silica Precipitation From Alkaline Silicate Solutions. Indian Pat. 67,664, appl. May 13, 1959 (to Council of Scientific and Industrial Research).

SiO₂ was precipitated in 98% yield by passing CO₂ through an alkaline silicate solution until the pH dropped to 9.

96. Samuel, T. The Removal of Silicic Acid From New Steam Generators. Mitt. Ver. Grosskesselbesitzer, No. 71, 1961, pp. 104-108.

Treatment with 5% H₂SO₄ and 5% H₂SO₄ - 2% NaF mixtures was much more effective in removing SiO₂ than was treatment with Na, K, or Li hydroxides or phosphates. Boiler pressure and steam output affected the silicic acid content of boiler water. The literature values of distribution coefficients of SiO₂ (steam/H₂O) were found to be too high.

97. Schumann, E. The Permissible Silicic Acid Content of Medium-Pressure Boilers. Mitt. Ver. Grosskesselbesitzer, No. 76, 1962, pp. 58-61.

The ratio of silicic acid in steam and water was used to give a coefficient that was compared with pressure inside the boiler. A quadratic function was obtained. Improved performance resulted from use of a newly determined safe maximum value for silicic acid content at various pressures and alkalinities.

98. Schwartz, M. C. Critical Problems in the Boiler Feedwater Field. J. Am. Water Works Assoc., v. 34, No. 8, 1934, pp. 1214-1226.

The solubilities of SiO₂, NaCl, NaOH, Na₂SO₄, and P₂O₅ in high-pressure, high-temperature steam are given. Methods of removing silica from boiler scale and turbine blade deposits are reviewed. The use of ferric and magnesium compounds and of dolomite is discussed.

99. Schwartz, M. C. The Removal of Silica From Water for Boiler Feed Purposes. The Ferric Sulphate and Hydrous Ferric Oxide Process. J. Am. Water Works Assoc., v. 30, No. 4, April 1938, pp. 659-678.

The reduction and removal of crystalloidal silica in natural waters can be accomplished by the use of salts of ferric iron, particularly the sulfate, with or without the addition of alkaline compounds and/or barium salts. The optimum pH is 8.5-9.5. The desilification may be carried out in conjunction with the cold or hot process of chemical softening.

The use of ferric iron compounds and alkaline reagents to produce hydrous ferric oxide in situ is more efficient for silica removal than the use of hydrous ferric oxide prepared separately from the process of water treatment.

100. Sharp, W. E. The Deposition of Hydrothermal Quartz and Calcite. Econ. Geol., v. 60, No. 8, December 1965, pp. 1635-1644.

The presently available data on the thermodynamic properties of water and the solubilities of quartz and calcite suggest the following conclusions:

(1) Both calcite and quartz can be deposited when two solutions of different temperatures are mixed at constant pressure.

(2) Quartz deposition should predominate over calcite above 300° C, but calcite should predominate at temperatures below 150° C when pressure-temperature changes in rising solutions cause the precipitation.

(3) Replacement of quartz by calcite and calcite by quartz may be caused by transport of CaCO_3 and SiO_2 along thermal gradients.

101. Siever, R. The Silica Budget in the Sedimentary Cycle. Am. Miner., v. 42, November-December 1957, pp. 821-841.

The source, transportation, and precipitation of silica in solution on and near the earth's surface are evaluated to arrive at the silica budget in sediments. The forms of silica stable at low temperatures and their solubilities are summarized. The primary source of silica in solution is the chemical weathering of silicate minerals formed at high temperatures and/or pressures. Formation and alteration of clay minerals in soils and hot springs are other sources. Marine

diagenesis of clays probably does not contribute much silica to solution. The major source of soluble silica in the early diagenesis of sediments is the dissolution of the remains of siliceous organisms. Solution of silica in deeply buried rocks is related to the pressure and temperature coefficients of solubility. Most natural waters are undersaturated with respect to amorphous silica and much of the ocean is undersaturated with respect to quartz. Hot spring and some soil waters may be supersaturated and inorganically precipitate silica, but the major mechanism for the precipitation of silica on the surface of the earth is biochemical. It is the diatoms, radiolaria, and other silica secreting organisms that are responsible for extracting silica from the sea. Crystalline quartz is precipitated from deep formation waters, given enough time. The silica cycle starts with the weathering of silicate minerals, goes through the stages of transportation and precipitation and, via metamorphism, comes back to reconstituted silicate minerals. The silica cycle in the past is discussed with reference to the development of the silica-secreting organisms and the conclusion is reached that, since the beginning of the Paleozoic and perhaps earlier, the silica cycle operated much as today.

102. Slavnyi, Yu A., and E. A. Vorob'eva. Precipitation of Silica From Soil Solutions at Freezing. *Pochvovedenie*, No. 9, 1965, pp. 80-84.

The precipitation of SiO_2 in lower soil levels is probably due to the freezing of solutions containing high concentrations of silica and is not related to any particular type of soil formation.

103. Styrikovich, M. A. Solubility of Impurities Present in Water and Steam and Their Behavior in the Steam Tract of Power Stations. *Tr. Mosk. Energ. Inst.*, 1955, No. 25, pp. 106-122; Abs. 14241 in *Ref. Zh.*, *Elektrotekh.*, 1956.

Both mechanical carryover of drops of water and solubility of substances in the steam are factors in the contamination of vapor in boiler water in high-pressure, cylindrical boilers. A mathematical expression is developed which expresses the relative importance of these processes. At pressures below 180 atm, the solubility of sodium salts is of less importance in their transfer to steam than for SiO_2 . Conditions necessary for the formation of a stable deposit are discussed.

104. Yakovleva, M. N., N. V. Saprykina, and G. A. Sidorenko. Coprecipitability of Aluminum and Silicic Acid in the System $\text{Al}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2\text{-H}_2\text{O}$ With Change in pH (In Connection with the Problem of the Origin of Bauxite). *Mineral'n. Syr'ye*, Moscow, Sb. No. 2, 1961, pp. 131-143; Abs. 5V434 in *Ref. Zh.*, *Geol.*, 1962.

A study was made of the effect of silicic acid in an acid solution of $\text{Al}_2(\text{SO}_4)_3$ on the composition of precipitate formed as a result of neutralizing the solution to final pH values of 3.0, 5.0, and 11.0. The $\text{Al}_2(\text{SO}_4)_3$ content was held constant; the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ was varied from 1:17 to 1:0.40. Al hydroxide and silicic acid coprecipitated readily. The amount of silicic acid in the precipitate depended on its concentration. At concentrations of ≤ 12.81 mg/l, silicic acid is stable over a wide range of pH. At alkaline pH's, the precipitates are mixtures of amorphous silica and gibbsite.

SOLUBILITY

The solubility of quartz has been studied by several investigators. Most of the research was done using only distilled water. The effect of salts such as sodium chloride and calcium chloride was studied by some investigators.

Research concerning the solubility of silicate minerals, such as serpentines, chlorites, etc., in saline water appears limited. Research concerning silicate clay mineral solubilities in saline environments would be useful.

Selected References

A. In Nonsaline Aqueous Media

105. Alexander, G. B. The Effect of Particle Size on the Solubility of Amorphous Silica in Water. J. Phys. Chem., v. 61, 1957, pp. 1563-1564.

The solubility of amorphous silica is related to the particle size by the equation $\log S = 4.80 \times 10^{-4} A - 2.043$, where S is the solubility in percent by weight in water at 25° C, and A is the specific surface area in square meters per gram. This solubility is affected by the amount of silanol (SiOH) groups in the internal structure of the silica polymer and by metal impurities. The surface energy of amorphous silica particles is estimated to be 1.1×10^{-6} cal/cm².

106. Alexander, G. B., W. M. Heston, and R. K. Iler. The Solubility of Amorphous Silica in Water. J. Phys. Chem., v. 58, June 1954, pp. 453-455.

The solubility of amorphous silica in water at 25° C is shown to involve an equilibrium between the solid phase and a monomeric form of silica in solution, presumably Si(OH)_4 . The same solubility (0.01 to 0.012%) was found using a suspension of finely divided amorphous silica powder and sols of colloidal particles of silica. The increase in total dissolved silica above pH 8 is shown to be due to the presence of (H_3SiO_4) ion in addition to Si(OH)_4 in solution. The concentration of Si(OH)_4 in equilibrium with the solid phase apparently is not affected by pH.

107. Anderson, G. M., and C. W. Burnham. The Solubility of Quartz in Supercritical Water. *Am. J. Sci.*, v. 263, June 1965, pp. 494-511.

The solubility of quartz in water has been determined by a weight-loss technique in the range 500° to 900° C and 1,000 to 10,000 bars. From the data, approximate values of ΔH (net heat change per mole for a given reaction) and ΔV (net volume change per mole for a given reaction) for the silica-water complex-forming reaction have been calculated, and assuming the complex to have the form $\text{SiO}_2(\text{H}_2\text{O})_n$, values of the partial molar volume of the solute have been calculated as a function of n, P, and T.

108. Baumann, H. Solubility of Silica in Water. *Beitr. Silikose-Forsch.*, No. 37, 1955, pp. 45-71.

Amorphous silica dissolves completely in water. Silicic acid polymerizes during the process and precipitates out as a gel once the solubility limit has been exceeded. Silicic acid activated with molybdate is soluble to the extent of 12-140 micrograms of SiO_2/cc at 30° C and a pH of 4.5 to 9. It is much more soluble in more alkaline solutions. It is assumed that crystalline forms of SiO_2 have similar solubilities.

The speed of solution of finely divided amorphous silica is low in strong acids and increases more than tenfold between pH 3 and 6. In contrast to the polymerization rate, it does not reach a maximum between pH of 6 to 7 but increases to a pH of 9 when it slows down.

The particle size of colloidal SiO_2 solution is extremely dependent upon treatment. Strong agitation greatly increases the "solubility" of the higher polyacids but does not affect the silicic acid activated with molybdate.

Results show that the solubility of medium-molecular-weight polyacids is unusually low--practically zero, so that the solution equilibrium occurs almost exclusively between colloidal particles

and very low-molecular-weight silicic acid. The solubility of the polyacids of middle molecular weights increases with decreasing pH. The concentration distribution shifts in favor of low-molecular-weight polysilicic acids with increasing pH--slowly below pH 9.6 (pK value of silicic acid) and markedly above pH 9.6.

109. Beckwith, R. S., and R. Reeve. Soluble Silica in Soils. 2. The Release of Monosilicic Acid from Soils. Australian J. Soil Res., v. 2, No. 1, 1964, pp. 33-45.

The release into solution of H_2SiO_3 from soils, clays, and synthetic Fe and Al oxides on which H_2SiO_3 had previously been adsorbed was lowest at pH 7-9 and increased with increasing acidity. Citrate aided the release. Most of the retention of H_2SiO_3 by soils is due to Fe and Al oxides. Finely-divided quartz and silica were unstable at near neutral pH values in the presence of excess Fe and Al oxides.

110. Frederickson, A. F., and J. E. Cox, Jr. Mechanism of "Solution" of Quartz in Pure Water at Elevated Temperatures and Pressures. Am. Miner., v. 39, 1954, pp. 886-900.

The solubilities of quartz in pure water at 200° to 370° C and at the supercritical pressure of 300 bars were measured in samples which were withdrawn from both the top and bottom of a solubility bomb. It was concluded that silica "dissolves" or disintegrates to give a colloidal suspension, with larger segregated particles contributing to apparent greater "solubility" in samples taken from the bottom of the bomb.

Electron-microscope photographs were made of the products of decomposition of quartz. The existence of a cementing material of the same composition but of different physical properties from the bulk of the crystal is postulated. The cementing material is thought to be preferentially removed during etching. A model is suggested to account for both the disintegration and regrowth of quartz.

111. Frederickson, A. F., and J. E. Cox. "Solubility" of Albite in Hydrothermal Solutions. Am. Miner., v. 39, 1954, pp. 738-749.

The apparent solubilities of an albite crystal in distilled water were determined at temperatures of 200°-350° C at 300 bars. Electron micrograph studies of evaporated solutions suggest a partial decomposition of the crystal into large, equant fragments of albite

and very small colloidal particles which form a gel. Upon cooling to room temperature and pressure, zeolite crystals form. Electrodialysis of the solutions suggest that four different kinds of sodium exist--the hydrated sodium ions in solution, the sodium ions in the hydration shell on the albite crystal, the sodium resulting from the breakdown of zeolite, and then from the breakdown of albite. The solubility of quartz is of the same order of magnitude as albite, indicating that quartz may decompose by the same mechanism. The somewhat greater solubility of quartz accounts for its first appearance in hydrothermal systems and its great persistence. It may be that the colloidal particles travel as such in and through rocks. They may contain as many as 1,000 unit cells of a silicate structure.

112. Friedman, I. Immiscibility in the System $\text{H}_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$. J. Am. Chem. Soc., v. 72, No. 10, October 1950, pp. 4570-4574.

Polybaric equilibria in the system $\text{H}_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$ was investigated at 400° and 450° C. One member of the immiscible pair reported at 250° to 350° has a critical endpoint with its coexisting gas at about 390° . Therefore, at 400° and 450° , the term liquid immiscibility no longer applies, although immiscibility still exists since the coexistent liquid and gas compositions are independent of the initial composition within the immiscible region.

113. Frondel, C. Stability of Colloidal Gold Under Hydrothermal Conditions. Econ. Geol., v. 33, No. 1, January-February 1938, pp. 1-20.

Colloidal silica protects colloidal gold both against electrolyte and against spontaneous coagulation by increase of temperature. The protection is accompanied by a reversal of charge of the sol in the presence of increasing concentrations of electrolyte.

The protecting action of silica against electrolyte for sols in the negative zone of stability increases with increasing temperature, and with increasing dilution of the gold sol.

Protected sols containing no added electrolyte are stable at 350° C, but coagulate spontaneously at 410° .

Silica sols are colloidal at 25° and 100° , and very probably up to 350° , in dilutions considerably under the solubilities recently reported by Hitchen and by Gruner. It is suggested that these investigators have measured a peptization equilibrium that simulates a true solubility, of the sort found for other hydrophilic colloids.

The origin and subsequent history of hydrothermal solutions is discussed with reference to the state in which gold is carried. In acid solutions, the gold is very probably transported in true solution. Part or all of the gold salt, however, may be carried as adsorbed electrolyte on colloidal silica present in the solution. With approaching neutrality or alkalinity of the originally acid solution, the gold is precipitated out as a sol, protected by colloidal silica.

114. Ganeev, I. G. Possible Form of the Transport of Silica in Hydrothermal Solutions. Sov. Geol., v. 6, No. 12, 1963, pp. 103-111.

The main form of transport of SiO_2 in hydrothermal solutions is believed to be accomplished by K and Na silicates in which the polymeric anion part of the molecule was formed by condensation of the $(\text{H}_3\text{SiO}_4)^-$ ions.

115. Goto, K. The Effect of pH on Polymerization of Silicic Acid. J. Phys. Chem., v. 60, July 1956, pp. 1007-1008.

In view of discordant results reported by earlier investigators, the effect of pH on the polymerization of silicic acid has been further studied. The reaction rate constant at various pH values in the range from 7 to 10 was calculated from the rate of disappearance of molecularly dispersed silica, on the assumption that the polymerization reaction is third order with respect to the concentration of molecular silica. The value of the calculated constant increased linearly with pH, indicating that the polymerization occurred more rapidly at higher pH. The time required for complete depolymerization of the particles of colloidal silica formed at various pH's indicated that larger particles are formed at higher pH.

116. Goto, K. States of Silica in Aqueous Solution. 2. Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.), v. 75, 1954, pp. 857-860.

The solubility of amorphous silica, as determined by a colorimetric method, was found to vary with pH and temperature. The coagulation of colloidal silica by sea water is discussed.

117. Greenberg, S. A. Thermodynamic Functions for the Solution of Silica in Water. J. Phys. Chem., v. 61, February 1957, pp. 196-197.

The thermodynamic functions connected with the equilibria between both high-surface-area amorphous silica and quartz and aqueous solutions saturated with monosilicic acid (H_4SiO_4) were calculated from data reported in the literature.

118. Greenberg, S. A., and T. N. Chang. Investigation of the Colloidal Hydrated Calcium Silicates. 2, Solubility Relationships in the Calcium Oxide-Silica-Water System at 25° . J. Phys. Chem., v. 69, No. 1, January 1965, pp. 182-188.

The solubilities of reaction mixtures of calcium oxide, silica, and water and of hydrated tricalcium silicate in water were investigated. It was concluded from the results that several solid phases exist in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ at 25°C : (1) Silica and silica that has partially reacted with calcium hydroxide at CaO-SiO_2 mole ratios less than 0.14, (2) partially reacted silica and CaH_2SiO_4 at mole ratios between 0.14 and 1, (3) CaH_2SiO_4 with varying amounts of calcium hydroxide dissolved in it for overall CaO-SiO_2 mole ratios greater than 1, and (4) $\text{CaH}_2\text{SiO}_4 \cdot n\text{Ca(OH)}_2$ and calcium hydroxide at overall CaO-SiO_2 ratios above about 1.75. The evidence for a phase $\text{Ca(H}_3\text{SiO}_4)_2$ is not conclusive. The solubility product for CaH_2SiO_4 and the ratio of the activity of the calcium hydroxide dissolved in CaH_2SiO_4 (in moles of calcium hydroxide per mole of CaH_2SiO_4) to that in the solution are constants which describe the system in the CaO-SiO_2 mole ratio range 1-1.75.

119. Harman, R. W. Aqueous Solution of Sodium Silicates. 1. Preparation and Electrical Conductivity. J. Phys. Chem., v. 29, 1925, pp. 1155-1168.

(1) Crystalline Na_2SiO_3 has been prepared and, from a solution of this salt, various other ratios $\text{Na}_2\text{O:SiO}_2$ have been prepared by removing the alkali electrolytically.

(2) Conductivity measurements have been made of ratios 2:1, 1:1, 1:5, 1:2, 1:3, and 1:4 at concentrations ranging from $2N_w$ to $0.005 N_w$.

(3) Solutions of 2:1 and 1:1 are excellent conductors; 1:2, 1:3, 1:4 are good conductors in dilute solution but abnormally low in concentrated solution.

(4) Hydrolysis into NaOH and colloidal silicic acid is not sufficient to account for this conductivity and calculations have been made of the mobility of the silicate ion.

(5) On plotting equivalent conductivity against ratio, there is only one change of direction and that a very sharp one at 1:2 in dilute solution; but, in concentrated solution, changes of direction also occur at 2:1 and 1:1.

(6) It appears likely that salts corresponding to 1:1 and 1:2 exist in solution; and that the other ratios are mixtures of these with NaOH or "hydrated" silica as the case may be.

(7) In concentrated solutions, either the extent of ionization and hydrolysis is very low, or aggregate or colloidal formation takes place.

120. Harman, R. W. Aqueous Solutions of Sodium Silicates. 2. Transport Numbers. J. Phys. Chem., v. 30, 1926, pp. 359-368.

(1) Transport numbers of sodium silicates of ratios 1:1, 1:2, 1:3, and 1:4 at concentrations ranging from 0.1 to 2.0 N_w have been measured by the Hittorf method, both electrode portions being analyzed for both sodium and silica.

(2) Ratio 1:1 evidently ionizes to Na^+ , OH^- , and SiO_3^{--} ions; n_{SiO_3} is small; n_{OH} , found by difference, is large.

(3) In ratios 1:2, 1:3, and 1:4, the transport number of the silicate ion is high, and the silicate anion contains more than 1 (SiO_2) per divalent charge; the average number of mols SiO_2 per divalent charge being equal to the ratio.

(4) The mobility of the SiO_3 ion in ratio 1:1 is about 70. In ratios 1:2, 1:3, and 1:4, it is approximately equal to that of the sodium ion, thus agreeing with mobilities calculated from conductivity experiments.

(5) In ratios 1:2, 1:3, and 1:4, the silicate anion is not the simple SiO_3^{--} ion, but is either an aggregation of simple silicate ions with or without colloidal silica or a definite complex silicate ion.

121. Harman, R. W. Aqueous Solutions of Sodium Silicates. 3. Sodium Ion Activity. J. Phys. Chem., v. 30, 1926, pp. 917-924.

(1) Measurements of sodium ion activity by means of a sodium amalgam electrode have been made for ratios 1:1, 1:2, 1:3, and 1:4, at concentrations ranging from 1.0-0.01 N .

(2) The activity coefficient γ has been plotted against the weight normality, N_w , and against the ratio Na_2SiO_2 .

(3) The curve of γ against N_w for ratio 1:1 passes through a minimum at a concentration lying between 0.1-0.2 N_w . The other curves show no minimum.

(4) In very dilute solution γ is high, but not so high as in corresponding concentrations of NaOH , whereas, in concentrated solutions of higher ratios, γ is abnormally low.

122. Harman, R. W. Aqueous Solutions of Sodium Silicates. 4. Hydrolysis. J. Phys. Chem., v. 30, 1926, pp. 1100-1111.

(1) Hydroxyl ion concentrations and percentage hydrolyses of silicate solutions of ratios, $\text{Na}_2\text{O}:\text{SiO}_2$, 2:1, 1:1, 1:1.5, 1:2, 1:3, 1:4, and at concentrations ranging from 2 to 0.01 N_w have been found by the hydrogen electrode method.

(2) The values of OH ion concentration and percentage hydrolysis have been plotted against the concentration and against the ratio $\text{Na}_2\text{O}:\text{SiO}_2$.

(3) None of these silicates are largely hydrolyzed. At 0.01 N_w , Na_2SiO_3 is only 27.8% hydrolyzed, while ratios 1:3 and 1:4 at the same concentration show only 1.5% hydrolysis.

(4) In concentrated solution, the percentage hydrolysis is very low.

(5) The liquid-liquid potential differences between these silicate solutions and KCl have been found by the Bjerrum extrapolation method.

(6) It appears probable that much of the silica is present as simple and complex silicate ions (and ionic micelles). This also accounts for the good conductivity and the high transport numbers.

123. Harman, R. W. Aqueous Solutions of Sodium Silicates. 5. Osmotic Activity, Lowering of Vapor Pressures and Freezing Points. J. Phys. Chem., v. 31, 1927, pp. 355-373.

(1) Measurements of the lowering of vapor pressure have been made by a dynamic method, for ratios $\text{Na}_2\text{O}:\text{SiO}_2$, 1:1 and 1:2 over a concentration range 0.1-2.5 N_w , and the results expressed in terms of the earlier ionic theory and also in terms of the more recent activity theory.

(2) Lowering of freezing points by the Beckmann Laboratory method have been found for ratios 2:1, 1:1, 1:2, 1:3, and 1:4 over a concentration range 0.01-2.0 N_w , and the results expressed in terms of the van't Hoff factor "i" and in terms of the activity theory.

(3) The results from vapor pressure and from freezing points are in fair agreement.

(4) Ratios 2:1 and 1:1, and to less degree 1:2, exhibit a high degree of osmotic activity, more especially in dilute solution. Ratios 1:3 and 1:4 show an abnormally low osmotic activity in concentrated solution but unexpectedly high in dilute solution.

(5) From the results, it appears that ratio 1:1 is the salt Na_2SiO_3 undergoing both hydrolytic and ionic dissociation giving rise to Na^+ , OH^- and SiO_3^{--} ions and H_2SiO_3 , most of the latter being crystalloidal. Na_2SiO_3 is practically completely dissociated in dilute solution but only 27.8% hydrolytically. Ratio 1:2 is the definite salt $NaHSiO_3$, behaving like Na_2SiO_3 and giving rise to Na^+ , OH^- and $HSiO_3^-$ ions and H_2SiO_3 . There is 0.60% dissociation at concentration 0.005 m but only 0.05% hydrolytic dissociation. The results from ratios 1:3 and 1:4 are not in accord with the view that these ratios are definite salts but agree well with the existence of complex aggregates in concentrated solution and of ionic micelle of the composition $(m.SiO_3.n.SiO_2aq.)^{m-}$ where $m + n/m = \text{ratio}$; the following equilibria also existing

124. Harman, R. W. Aqueous Solutions of Sodium Silicates. 6. Heterogeneous Equilibria System: $Na_2O:SiO_2:H_2O$ at 25° . J. Phys. Chem., v. 31, 1927, pp. 511-518.

(1) Previous work in this field has been surveyed and summarized.

(2) An investigation of the ternary system $Na_2O:SiO_2:H_2O$ at $25^\circ C$ has been carried out and the results shown graphically.

(3) Towards the $H_2O:SiO_2$ side of the system, the solutions became colloidal and so invalidated further work.

(4) Two compounds only are indicated as stable in solution-- $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$.

(5) Na_2SiO_3 crystallizes with 9, 6, and 2.5 H_2O ; $Na_2O \cdot 2SiO_2$ with $9H_2O$.

125. Harman, R. W. Aqueous Solution of Sodium Silicates. 7. Silicate Ions. Electrometric Titrations: Diffusion: Colorimetric Estimation. J. Phys. Chem., v. 31, 1927, pp. 616-625.

(1) Electrometric titrations of 0.1 and 0.2 N_w . Na_2SiO_3 with 0.1 N and 1.219 N . HCl , and 0.2 N_w . Na_2SiO_3 , 1:4, with 10 N . $NaOH$ have been carried out.

(2) The curves obtained with Na_2SiO_3 and HCl are typical of dibasic acids, thus suggesting H_2SiO_3 as dibasic with salts $NaHSiO_3$ and Na_2SiO_3 .

(3) The primary and secondary dissociation constants have been calculated from hydrolysis results and from these electrometric titrations; $k_1 = 4.2 \times 10^{-10}$ and $k_2 = 0.51 \times 10^{-16}$.

(4) The amount of crystalloidal silica in ratios 2:1, 1:3, and 1:4 has been compared with that in ratio 1:1 in very dilute solution by means of the colorimetric test with H_2SO_4 and ammonium molybdate.

(5) In very dilute solution, most of the silica in these ratios is crystalloidal, but increase of concentration and increase of ratio increase the colloidal content.

(6) Diffusion experiments through membranes of collodion and parchment paper indicate that most of the silica in ratios 1:1 and 1:2 is diffusible; about two-thirds of the silica in 0.3 N_w 1:4, and about one-third in 1.0 N_w H_2SiO_3 was crystalloidal.

(7) H_2SiO_3 is much stronger than hitherto supposed, due no doubt to the fact that, when prepared by continuous dialysis, the ionizable and diffusible portion is lost.

126. Harman, R. W. Aqueous Solutions of Sodium Silicates. 8. General Summary and Theory of Constitution. Sodium Silicates as Colloidal Electrolytes. J. Phys. Chem., v. 32, 1928, pp. 44-60.

(1) A summary is given of the results and conclusions of seven preceding papers on the aqueous solutions of sodium silicates of ratios 2:1 to 1:4 at concentrations ranging from 0.001 N_w to 2.0 N_w , from the points of view of conductivity, transport numbers, sodium ion activity, hydrolysis, osmotic activity, phase rule, and crystalloidal silica.

(2) The various data have been correlated and an explanation given of the constitution and behavior in aqueous solution of these silicates.

(3) The evidence for crystalloidal silica and silicate ions has been recapitulated.

(4) Ratios 1:1 and 1:2 only are definite salts, namely, Na_2SiO_3 and NaHSiO_3 , and their percentage hydrolysis and ionization have been found and shown to agree with the various measurements. This affords a complete explanation of their behavior in solution.

(5) Above ratios 1:2 colloidal silica is in evidence, the proportion of colloidal silica increasing with the concentration and the ratio $\text{SiO}_2:\text{Na}_2\text{O}$.

(6) In dilute solutions of ratios above 1:2 crystalloidal uncharged silica probably H_2SiO_3 or simple hydrated silica occurs.

(7) These ratios higher than 1:2 exhibit properties characteristic of colloidal electrolytes with a micelle of the composition $(m\text{SiO}_3 \cdot n\text{SiO}_2 \cdot aq.)^m$, where $\frac{m+n}{m} = \text{ratio SiO}_2/\text{Na}_2\text{O}$.

(8) In concentrated solutions of the higher ratios, a large colloidal aggregate exists, containing both sodium and silica.

(9) Silicic acid has been shown to be stronger than usually supposed, its dissociation constants being of the order 10^{-10} and 10^{-16} .

127. Heitmann, H. G. Solubility of Silica in Water and Water Vapor. Glustech. Ber., v. 38, No. 2, 1965, pp. 41-54.

The solubility of SiO_2 hydrogel and of quartz powder at 20° - 650° C and at pressures of 6-300 kg/cm^2 was determined.

128. Hitchen, C. S. A Method for the Experimental Investigation of Hydrothermal Solutions, With Notes on Its Application to the Solubility of Silica. Trans. Inst. Min. and Met., v. 44, 1935, pp. 255-336.

Solubilities of silica in water, determined by a new technique in newly designed apparatus, were found to increase with temperature from 100° to 325° C. Solubilities in aqueous Na metasilicate decreased with increase in temperature.

129. Hitchen, C. A. The "Solubility" of Silica. *Econ. Geol.*, v. 40, 1945, pp. 361-365.

Studies of "solubility" of silica made by various workers, including G. C. Kennedy, indicate that silica has no true molecular solubility. It appears that all forms of silica in pure water exhibit a "peptization solubility" which, at a given temperature, involve a twofold equilibrium between the solid phase, singly dispersed molecules, and colloidal aggregates: solid phase $\rightleftharpoons$ simple molecular dispersion $\rightleftharpoons$ colloidal dispersion. The crystallization of quartz in nature is dependent upon the presence of small quantities of alkali and, possibly, other as yet undetermined impurities.

130. Holt, P. F., and D. T. King. Solubility of Silica. *Nature*, v. 175, No. 4455, Mar. 19, 1955, pp. 514-515.

Experimental evidence is offered which indicates that the portion of silica that dissolves in water rapidly is due to an incomplete monolayer of adsorbed silicic acid on the silica surface.

131. Iwasaki, I., T. Tarutani, T. Katsura, and H. Arino. Silica in Water. 1. Relation Between Ionic and Colloidal Silica. *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), v. 75, 1954, pp. 857-860.

The equilibrium between ionic and colloidal silicic acid was found in a study of sodium silicate solution to be affected by pH and temperature but not by concentration of silicic acid. At 100° C, all the silicic acid is in ionic form, regardless of pH.

132. Jephcott, C. M., and J. H. Johnston. Solubility of Silica and Alumina. *Arch. Ind. Hyg. and Occupational Med.*, v. 1, No. 3, March 1950, pp. 323-340.

All forms of alumina markedly depress the solubility of quartz and diatomaceous earth. The greatest degree of depression is exerted by those types of alumina whose own solubilities are the least affected by the action of silica.

133. Kahlenberg, L., and A. T. Lincoln. Solutions of Silicates of the Alkalies. *J. Phys. Chem.*, v. 2, 1898, pp. 77-90.

The freezing points and electrical conductivities of solutions of the silicates of sodium, potassium, lithium, rubidium, and cesium show that these salts are hydrolized by water into colloidal silicic

acid and the hydroxide of the alkali metal. For silicates of the general formula M_2SiO_3 , $MHSiO_3$, and $M_2Si_5O_{11}$, the degree of hydrolysis is practically complete when the dilution reaches 1 gram molecule of the salt per 48, 48, and 128 liters of solution, respectively. Greater dilution results in even more complete hydrolysis. Since almost all natural waters contain silicates in lower concentrations than these amounts, silicic acid most always occurs in natural waters in the colloidal state.

134. Kane, J. C., V. K. La Mer, and H. B. Linford. The Effect of Solid Content on the Adsorption and Flocculation Behavior of Silica Suspensions. J. Phys. Chem., v. 68, No. 12, December 1964, pp. 3539-3544.

This research analyzes the authors' previously published results on flocculation in the silica-polymer system by considering both the theory of Smellie and La Mer and the modification of Healy and La Mer, which treats the adsorption phenomenon more fundamentally. The variation of P_m at decreasing solid content is explained in terms of secondary adsorption resulting from the increased time intervals between unit floc-unit floc collisions. A method for calculating b , the ratio of rate constants for the adsorption and desorption processes, and θ , the fraction of the solid surface covered, as a function of added polymer concentration, is outlined. An analysis of the deviations from the eighth power filtration law in terms of b is also presented. The basic assumption that the adsorption mechanism obeys a Langmuir-type equation has been justified. Preliminary calculations are included to indicate the geometrical dimensions that exist when flocculation occurs in the silica-polymer system.

135. Kot, A. A., and A. A. Pshemenskii. The Solubility of Quartz and Sodium Metasilicate in Super-Heated Steam. Elek. Stant., v. 28, No. 2, 1957, pp. 14-19.

The solubility of SiO_2 and Na_2SiO_3 was measured in an experimental apparatus designed to duplicate the conditions between the inlet and outlet valves of a turbine. Solubility of SiO_2 increased from 0.017 to 10.4 mg/kg with an increase in temperature from 207° to 567° C and an increase in pressure from 1 to 180 atm. Lowering the SiO_2 content to 0.02-0.025 mg/kg and increasing the alkali-silica ratio led to a lowering of the deposition of silicic acid on the turbine blades. Below 0.015-0.017 mg/kg, no deposition occurred.

136. Kartvelishvili, G. Ya. Hydrochemical Features of the Chorchan Area Talc Deposit. Tr. Gruzinsk. Politekhn. Inst., No. 1, 1960, pp. 83-89. Abs. 3G139 in Ref. Zh., Khim., 1962.

Underground waters of this area are of the bicarbonate type and differ only in cation composition. Mg predominates in waters associated with serpentine and talc deposits.

137. Kennedy, G. C. The Hydrothermal Solubility of Silica. Econ. Geol., v. 39, 1944, pp. 25-36.

The solubility of silica glass in water was determined at 200° to 420° C at a pressure of 300 atmospheres by measuring the loss of weight of sintered bundles of SiO₂ glass threads. An Allegheny 44 steel bomb of 155 cc capacity was used. The solubility rose from essentially zero at temperatures below 200° C to 0.20 part of silica per 100 parts of water at 360° C and decreased to 0.10 part per 100 parts of water at 420° C. Some previous investigations of solubility of silica in water, it is believed, indicated too great a solubility as a result of failure to distinguish true solubility from colloidal dispersion.

Solubility in the vapor phase of water appears to be a function of the density of the vapor phase as well as of temperature. At high pressures, as the density of the vapor phase approaches that of the liquid, its ability to act as a solvent will approach that of the liquid.

138. Kennedy, G. C. A Portion of the System Silica-Water. Econ. Geol., v. 45, 1950, pp. 629-653.

The solubility of quartz plates in water was measured at temperatures ranging to 610° C and at pressures ranging to 1,750 bars. A steel bomb made resistant to corrosion by exposure to air at 600° C was used. Rate of solution of the quartz plates depended on temperature, orientation of the quartz plate and on minute compositional differences in quartz. The solubility determinations were made along the three-phase boundary, quartz-gas-liquid; and in two two-phase fields, quartz-liquid and quartz-gas. No break was encountered in the solubility curves as they crossed the boundary between the quartz-gas and quartz-liquid fields, provided that the specific volume of the fluid phase was held constant.

The solubility of quartz in water was much lower than is the solubility of quartz glass or colloidal silica in water.

Precipitation of silica upon release of pressure at high temperatures may be an important factor in geological deposition of minerals.

139. Kennedy, G. C., G. J. Wasserburg, H. C. Heard, and R. C. Newton. The Upper Three-Phase Region in the System $\text{SiO}_2\text{-H}_2\text{O}$. *Am. J. Sci.*, v. 260, Summer 1962, pp. 501-521.

Melting relations in the system $\text{SiO}_2\text{-H}_2\text{O}$ were studied at high temperatures and pressures. A quadruple point for the equilibrium among quartz, tridymite and two fluids was found at $1,160^\circ\text{C}$ and 1,500 bars. A second quadruple point for tridymite, two fluids and cristobalite is estimated to be near $1,470^\circ\text{C}$ and 400 bars. The freezing point of SiO_2 in equilibrium with two fluid phases is depressed from $1,720^\circ\text{C}$ at one bar to $1,130^\circ\text{C}$ at 2,000 bars. This freezing point is diminished by only an additional 50°C with a further increase in pressure to 9,700 bars. The compositions of coexisting fluids along the upper three-phase boundary have been determined. A critical endpoint for the univariant equilibrium curve was found at $1,080^\circ\text{C}$ and 9,700 bars with a composition of approximately 75 weight-percent SiO_2 to 25 weight-percent H_2O .

140. Kitahara, S. Polymerization of Silicic Acid Obtained by the Hydrothermal Treatment of Quartz and the Solubility of Amorphous Silica. *Rev. Phys. Chem. Japan*, v. 30, No. 2, 1960, pp. 131-137.

The rate of polymerization was greatest at pH 7.5. Activation energy was calculated to be 9.8 kcal/mole at pH 6.0. The heat of solution of amorphous silica was 3.2 kcal/mole.

141. Kitahara, S. Solubility of Quartz in Water at High Temperatures and Pressures. *Rev. Phys. Chem. Japan*, v. 30, 1960, pp. 109-114.

Solubilities measured up to 500°C and 900 atm, were 10% lower than those previously reported. With certain exceptions, solubility was proportional to fugacity above the critical temperature.

142. Krauskopf, K. B. The Geochemistry of Silica in Sedimentary Environments. Paper in Silica in Sediments Symposium. Soc. Econ. Paleontologists and Miner., Spec. Pub. 7, 1959, pp. 4-19.

Amorphous silica dissolves in either fresh or marine water to the extent of 100-140 ppm at ordinary temperatures. This is true solution, not colloidal dispersion, most or all of the silica being in the form of monosilicic acid, H_4SiO_4 . Crystalline forms of silica have lower solubilities, quartz least of all. The solubility increases as temperature rises, but is little affected by changes of pH in the range 0-9.

Silica ordinarily does not precipitate at once from supersaturated solutions, but forms a colloid. In concentrated solutions, the colloid may eventually set to a gel or precipitate as flocculent masses, but in fairly dilute solutions the dispersed sol is very stable. At equilibrium, the sol contains dissolved silica in amounts given by the figures above, in addition to the colloidal particles. The reactions of forming and disaggregating the sol particles are slow, so that supersaturated solutions of molecularly dispersed silica and very dilute solutions of colloidal silica can persist for days or weeks.

Colloidal silica may be precipitated by evaporation, by cooling, or by addition of electrolytes, but if the solution is at equilibrium the dissolved part of the silica does not precipitate. Precipitation of dissolved silica may be brought about by organisms, by adsorption, by reaction with cations to form silicates, and probably by slow approach to equilibrium with a crystalline form of silica.

In natural waters silica is mostly in true solution. Its concentration is less than the amount at equilibrium with amorphous silica, both because it is derived largely from materials less soluble than amorphous silica and because it is removed from solution by the processes described above. Most precipitated silica is disseminated widely through sediments. To form chert requires an unusually abundant supply, diagenetic redistribution of freshly precipitated silica, or later replacement.

143. Lenher, V., and H. B. Merrill. The Solubility of Silica. J. Am. Chem. Soc., v. 39, 1917, pp. 2630-2638.

The solubility of silica has been determined in water and in hydrochloric and sulfuric acids. The solubility is definite and depends on the temperature and concentration.

With gelatinous silica, equilibrium is reached in a few hours, or at most a few days. With ignited silica, equilibrium cannot be attained in days or weeks.

The solubility of gelatinous silica is the same, no matter how the gel is prepared. The true solubility of ignited silica is probably the same as that of gelatinous silica, but as saturation is not reached in any short period of time, the apparent solubility is somewhat less than that of gelatinous silica.

144. Lyon, S. R. Investigations in the Systems $\text{SiO}_2\text{-H}_2\text{O}$ and Co-SiO_2 . M.S. Thesis, Miami Univ., Oxford, Ohio, 1964, 63 pp.

Samples of amorphous silica were reacted at fixed water vapor pressures and temperatures for various lengths of time. For purposes of comparison, amorphous silica was also heated (dry) at high temperatures. The sequence of phases developed was compared to a similar sequence developed with cobalt as a trace additive in silicic acid.

In general, the appearance of phases developed under hydrothermal conditions follows the known sequence: cristabolite $\rightarrow$ keatite $\rightarrow$ quartz. The survival time of cristabolite decreases with increasing temperature until, at 15,000 psi and 600° C, it becomes zero. Keatite is a persistent metastable phase throughout the temperature range investigated.

The presence of trace amounts of cobalt decelerates the rate of formation of cristabolite and slows the rate of conversion rate of silicic acid to quartz.

145. Millot, G. Silica, Silixite, Silicification, and Growth of Crystals. Bull. Serv. Carte Geol. Alsace Lorraine, No. 13, 1960, pp. 129-146.

This is a review with 52 references, which include material on the solubility of silica in waters and rock silicification.

146. Morey, G. W., and W. T. Chen. The Action of Hot Water on Some Feldspars. Am. Miner., v. 40, 1955, pp. 996-1000.

Hot water was passed over the feldspars contained in closed bombs, the total amount of solution was weighed and analyzed, and the material remaining in the bomb was studied with X-rays and the petrographic microscope. At 350° C and 5,000 psi, the solution obtained from orthoclase and from albite contained over 90% of the dissolved material in the feldspar ratio. At lower temperatures and pressures, 200° C and 2,000 psi, and 100° C and 40 psi, albite was decomposed in greater proportion. At 350° C and 2,000 psi, a large amount of analcime was found in the albite experiment, but none was found at the lower temperatures.

147. Morey, G. W., R. O. Fournier, J. J. Hemley, and J. J. Rowe. Field Measurements of Silica in Water from Hot Springs and Geysers in Yellowstone National Park. U.S. Geol. Survey, Prof. Paper 424-C, 1961, pp. 333-336.

The dissolved silica and total silica content of waters were determined immediately after collection and then again after standing for several hours, 1 day, 3 days, 4 days, and several weeks. The pH was also determined. An attempt to correlate present chemical composition with composition determined previously was hindered by the effects of an intervening earthquake.

148. Morey, G. W., R. O. Fournier, and J. J. Rowe. The Solubility of Amorphous Silica at 25° C. *J. Geophys. Res.*, v. 69, No. 10, May 15, 1964, pp. 1995-2002.

Solutions in contact with solid amorphous silica at room temperature tend to become supersaturated. Experiments carried out over long periods show that steady states of supersaturation, 120 to 170 ppm, may persist for months. Eventually, however, the colorimetrically detectable dissolved silica in contact with silica gel decreases to about 115 ppm. Dissolved silica in waters collected from hot springs (pH range 6.0 to 8.5) also slowly polymerizes and approaches 115 ppm. Extrapolation to 25° C of solubility data taken at high temperatures also yields a value of about 115 ppm for the solubility of amorphous silica. It is concluded that in nearly neutral solutions 115 ppm is the solubility of amorphous silica at 25° C, the differential heat of solution, ΔH , is 3.35 kcal/mole, and the standard free energy of solution, $\Delta F^\circ_{25^\circ \text{C}}$, is approximately 3.7 kcal/mole.

149. Morey, G. W., R. O. Fournier, and J. J. Rowe. The Solubility of Quartz in Water in the Temperature Interval from 25° to 300° C. *Geochim. et Cosmochim. Acta*, v. 26, 1962, pp. 1029-1043.

The solubility of quartz in water was investigated by three sets of experiments: (1) at 1,000 atm P_{H_2O} and temperatures ranging from 45° to 300° C; (2) at water pressures appropriate for the coexistence of three phases, gaseous water, liquid, and quartz, at temperatures ranging from 69° to 240° C; and (3) a long-term study of the dissolution of quartz grains that were continuously tumbled in water at room temperature.

Saturated silica solutions in equilibrium with quartz were obtained in a few days at temperatures above 100° C.

At room temperature and pressure, highly supersaturated silica solutions were obtained by continuously rotating quartz grains and water in plastic bottles at 75 rpm. In one run, the amount of silica in solution increased to a maximum value of 395 ppm after

370 days. Another run reached 80 ppm silica after 386 days and then dropped to 6 ppm silica. It is concluded that 6 ppm is essentially the true solubility of quartz at 25° C.

Quartz grains and silica glass grains, continuously rotated in water at 1/2 rpm for 1 year each, contributed less than 1 ppm of colorimetric silica.

Two significant factors that may have contributed to the formation of supersaturated silica solutions in the runs rotated at 75 rpm at room temperature are (1) stresses and structural irregularities at the surfaces of the crushed quartz grains, which contributed silica into solution more readily than well crystallized quartz, and (2) the very slow rate at which dissolved silica polymerizes to species appropriate to act as nuclei for quartz growth.

150. Morey, G. W., and J. M. Hesselgesser. The Solubility of Some Minerals in Superheated Steam at High Pressures. *Econ. Geol.*, v. 46, 1951, pp. 821-835.

An apparatus and method for determining solubility of solids in superheated steam at high pressures are described. Measurements were made at 400°, 500°, and 600° C and at pressures up to 2,000 bars. Materials studied include quartz, silica glass, albite, microcline, enstatite, anhydrite, barite, anglesite, sodium sulfate, hematite, and some sulfides.

151. Mosebach, R. The Hydrothermal Solubility of Quartz as a Heterogeneous Gas Equilibrium. *Neues Jahrb. Mineral., Abhandl.*, v. 87, No. 3, March 1955, pp. 351-388.

The solubility of quartz in all conditions of the hydrothermal range can be expressed by two equations, which, within the limit of experimental error of the difficult quantitative studies, agree with the data of various workers in the field: (1) an interpolation equation, $\log L = 2 \log D + 0.004 T - 2.13$; and (2) an equation of state, $\log L = 2 \log D - (2.71/T) + 3.68 \text{ g SiO}_2/\text{kg H}_2\text{O}$, where L is the solubility, T is absolute temperature, and D is the density. Values obtained at various temperatures permitted construction, using equation 2, of a number of curves (isotherms at various densities and concentrations or pressures and concentrations; isobars at various temperatures and concentrations; isolytes at various temperatures and concentrations or temperatures and pressures). Also, a limiting curve for two phases was constructed.

Within the experimental conditions, the hydrothermal solubility of quartz is a bimolecular gas reaction, which follows the following equation: $\text{SiO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons [\text{Si}(\text{OH})_4]$. The differential heat of solution of quartz in water is -9,500 cal/mols SiO_2 .

152. Mosebach, R. Thermodynamic Behavior of Quartz and Other Forms of Silica in Pure Water at Elevated Temperatures and Pressures With Conclusions on Their Mechanism of Solution. J. Geol., v. 65, No. 4, 1957, pp. 347-363.

The solution mechanism of β -quartz in water at elevated pressures and temperatures corresponds to a bimolecular, heterogeneous gas reaction. The reaction is described by the equation

Silica is dispersed at least to molecules, probably to ions. Condensation or polymerization during the hydrothermal equilibrium state seems to be excluded. From 200° to 600° C and pressures up to 2,000 bars, the hitherto experimentally determined solubility of β -quartz is reproduced by the following formula:

$$\gamma(\text{SiO}_2) = D^2 e^{(Q/RT + h)},$$

in which Q signifies the differential solution enthalpy of β -quartz in water and has the value $Q_Q = -9,470$ cal/mole SiO_2 ; $h = 0.362$.

The solubility values of silica glass and precipitated silica are also in part reproduced by the foregoing equation. Their differential solution enthalpy has the value $Q_g = 12,250$ cal/mole SiO_2 , while $h = 3.337$. The difference between Q_Q and $Q_g - \Delta Q$ amounts to about -2,800 cal/mole SiO_2 and corresponds to the melting enthalpy of β -quartz, Q_s , which is determined to be about -3,200 to -3,400 cal/mole SiO_2 , as is theoretically required. Silica glass in a hydrothermal environment also seems to be dispersed at least to $[\text{Si}(\text{OH})_4]$; only precipitated silica (Straub, 1946) also shows partly $[\text{SiO}(\text{OH})_2]$ at very low H_2O pressures or H_2O densities. Its solubility formula, therefore, is

$$\gamma(\text{SiO}_2) = D^{5/3} e^{(Q/RT + h)}.$$

Finally, new experimental results, given by Frederickson and Cox (1954), are referred to. Their conclusions, partly contradictory to the foregoing, are examined critically, and an explanation is attempted.

153. Mueller, P. Hydrothermal-Synthetic Investigations in Alpine Serpentinities in Connection With an Observed Paragenesis of Minerals. Neues Jahrb. Mineral., Monatsh., No. 1, 1964, pp. 17-21.

Aqueous mixtures of serpentinite and grossular were heated for 300 hours at 500° C and 1,000 atm. Studies were made of the equilibria between serpentine and chlorite and between grossular and chlorite.

154. Roller, P. S., and G. Ervin, Jr. The System Calcium Oxide-Silica-Water at 30°. The Association of Silicate Ion in Dilute Alkaline Solution. J. Am. Chem. Soc., v. 62, No. 3, Mar. 9, 1940, pp. 461-471.

Hydrated calcium silicates are gelatinous. The effects to be expected from this in a phase rule study are discussed briefly.

Measurements were made of the ratio of CaO to SiO₂ in the solid phase and of the concentrations of CaO and SiO₂ in solution at 30.2° C. Equilibrium and reversibility were tested for.

Four phase ranges were distinguished; in two of these the concentrations were invariant. Adsorption of CaO by the solid phases occurred throughout. The compositions of the hydrated compounds, deduced from considerations of adsorption isotherm and solubility product constant, were (1) CaO·SiO₂ (CaH₂SiO₄), (2) 3CaO·4SiO₂ (Ca₃(HSi₂O₆)₂), (3) CaO·2SiO₂ (indifferently either CaH₂Si₂O₆ or Ca(HSiO₃)₂). The invariant concentrations for the mixture of (1) and (2) were 3.09 millimoles CaO/l and 0.090 millimole SiO₂/l and, for the mixture of (2) and (3), 0.900 millimole CaO/l and 0.931 millimole SiO₂/l.

The assumed exclusive presence of the simple ions SiO₃⁼ and HSiO₃⁻, or in the more rational and preferred orthosilicate terminology, H₂SiO₄⁼ and H₃SiO₄⁼, was inconsistent with the existence of the only alternatives of Ca(H₃SiO₄)₂ or any reasonable double compounds of the latter with CaH₂SiO₄. It was necessary to assume, therefore, that association took place in the dilute alkaline solutions. The postulate of two sets of silicate ions, based on an association equilibrium between H₃SiO₄⁼ and H₂Si₂O₆⁼, led to reasonable and concordant results. The association constant, solubility product constants, and one of the ionization constants, were calculated to a known precision. A high tendency toward association is evidenced.

155. Roy, C. J. Silica in Natural Waters. Am. J. Sci., v. 243, No. 7, July 1945, pp. 393-403.

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.

156. Shimada, K., and K. Kikuno. Water-Soluble Silica. Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.), v. 81, 1960, pp. 426-428.

The solubility at room temperature of powdered samples of siliceous rocks and diatomaceous earth ranged from 0.02 to 0.05 mg SiO_2/ml of water. The solubility of silica gel was about 0.59 SiO_2/ml of water. Heat treatment of the rocks had almost no effect.

157. Sprauer, S. W., and D. W. Pearce. Equilibria in the Systems $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 25°C . J. Phys. Chem., v. 44, 1940, pp. 909-916.

(1) The system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ has been investigated at 25°C from the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ equal to 1:1 up to 36 percent Na_2O by weight.

(2) The phase diagram shows, in several places, marked differences from that derived from the work of previous investigators. In particular is the field of stability of $\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot 6\text{H}_2\text{O}$ at lower Na_2O concentrations than reported by Harman.

(3) Evidence for the compound $3 \text{Na}_2\text{O}\cdot 2\text{SiO}_2\cdot (11?)\text{H}_2\text{O}$ at stable equilibrium is presented; lower hydrates may exist at somewhat higher temperatures and concentrations.

(4) Some data on the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 25°C are presented.

158. Steinour, H. The System $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ and the Hydration of Calcium Silicates. *Chem. Rev.*, v. 40, 1947, pp. 391-460.

A review is given of various investigations of the system $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ at ordinary temperatures, with 191 references.

159. Stöber, W. Theoretical Aspects of the Dissolving Process of SiO_2 Preparations and of SiO_2 Minerals. *Beitr. Silikose-Forsch.*, Sonderband, v. 1, 1955, pp. 43-48.

The stability of unimolecular solutions of SiO_2 , the condensation of such molecules, and the effect of pH and presence of anions are discussed.

160. Tuttle, O. F., and I. I. Friedman. Liquid Immiscibility in the System $\text{H}_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$. *J. Am. Chem. Soc.*, v. 70, No. 3, 1948, pp. 919-926.

A portion of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ was investigated. Equilibrium relations were determined at 250° , 300° , and 350°C . The system possesses liquid immiscibility with a lower consolute temperature between 200° and 250°C . The immiscible region is intersected at 250° by the quartz stability field, and at 300° and 350° by the stability fields of quartz and $\text{Na}_2\text{Si}_2\text{O}_5$.

161. Van Nieuwenberg, C. J., and P. M. Van Zon. Semiquantitative Measurements of the Solubility of Quartz in Supercritical Steam. *Rec. trav. Chim.*, v. 54, 1935, pp. 129-132.

The solubility of quartz in supercritical steam has been approximately determined at 380° , 400° , and 425°C and at pressures ranging from 300 to 500 atm. The p-x-diagrams obtained are in accord with theoretical predictions. This result must remove any reasonable doubts as to the reality of the phenomenon.

162. Wawrik, F. Silica Regimen and Diatomaceous Vegetation in the Lunz Lake and Neighboring Streams. *Internat. Ver. Theoret. und Angew. Limnol.: Verhand.*, v. 14, pt. 1, 1959 (pub. 1961), pp. 182-185.

The effects of depth, presence of diatomaceous vegetation, and seasonal variation on the silica content of an alpine lake and its tributary streams are discussed.

163. Weill, D. F., and W. S. Fyfe. The Solubility of Quartz in H₂O in the Range 1000-4000 Bars and 400-550° C. *Geochim. et Cosmochim. Acta*, v. 28, 1964, pp. 1243-1255.

The solubility of quartz in H₂O has been measured between 1-4 kbar at 400°, 450°, 500°, and 550° C. Two rate studies at 400° and 625° C are consistent with an equation of the form $dx/dt = a - bx$ for the rate of solution of quartz in H₂O, where x is the concentration of SiO₂ in solution at time t . The temperature dependence of the two specific rate constants, a and b , give values of approximately 16.5 and 14.5 kcal/mole for the activation energies of the dissolution and crystallization processes, respectively. The temperature and pressure dependence of solubility used in conjunction with the most widely accepted reaction for the solution of quartz, $\text{SiO}_2(\text{qtz}) + 2\text{H}_2\text{O} \rightleftharpoons \text{Si}(\text{OH})_4$, lead to thermodynamic calculations indicating unreasonable behavior of the assumed solute species. It is suggested that these anomalies may reflect the inability of the accepted solution reaction to represent the heterogeneous equilibrium between quartz and solution over a large range of temperature and pressure.

B. In Saline Aqueous Media

164. Atkins, W. R. G. Seasonal Changes of the Silica Content of Natural Waters in Relation to Phytoplankton. *J. Marine Biol. Assoc. U. K.*, v. 14, 1926, pp. 89-99.

(1) The method of Diénert and Wandenbulcke permits the estimation of silicate in solution down to the limit of 0.04 mg of silica per liter, which cannot be distinguished from zero. The phosphate normally present does not interfere with the reaction.

(2) All fresh waters examined were found to contain more silicate than does the water of the English Channel.

(3) The water of Plymouth Sound is richer in silicate than that of the sea.

(4) At Station E1 in the English Channel, silicate decreases during spring from a winter maximum of 200-240 mg per cubic meter so that, from April to June 1925, the amount left, recorded as 40 mg per cubic meter, was indistinguishable from zero. At this time, the water was stripped of phosphate also. Silicate increased again till early July, decreased in August and again in November; the times of decrease are suggested as being those of diatom increase.

(5) In deep Atlantic water, silicate is much more abundant than in English Channel; values from 360 mg per cubic meter at 1,000 meters to 1,200 mg at 3,000 meters were obtained. In winter at any rate, the surface value in the Atlantic is similar to that off Plymouth about 110 mg per m³ in 1925.

165. Atkins, W. R. G. Seasonal Variations in the Phosphate and Silicate Content of Sea Water During 1926 and 1927 in Relation to the Phytoplankton Crop. *J. Marine Biol. Assoc. U.K.*, v. 15, No. 1, February 1928, pp. 191-205.

Sunshine rather than wind seems to be a factor during periods when the spring diatom outburst causes phosphate depletion of surface sea water. Diatom outbursts need not originate near the coast. The spring decrease in phosphate and silicate shows good agreement, but a summer rise in silicate has been observed while phosphate remains low. The silicate content may vary from year to year at certain sampling stations. Phosphate regeneration may take place near the surface more rapidly than at intermediate depths; the bottom is the most important source of phosphate.

166. Bartholomé, P. Effect of Dissolved SiO₂ on the Conditions of Dolomite Formation. *Compt. rend.*, v. 260, No. 20, Groupe 9, May 17, 1965, pp. 5307-5309.

Studies were made of the influence of the activity of SiO₂ in sea and lake waters on the repartition of Mg between carbonated and argillaceous fractions of sediments, as represented by talc. Several thermodynamic equilibria were considered. The concentration of SiO₂ determines whether dolomite is stable or unstable.

167. Butuzov, V. P. Artificial Quartz. *Cesk. Casopis Fys.*, v. 12, 1962, pp. 105-112.

Solubility of SiO₂ in 5% Na₂CO₃ and in K₂CO₃ was determined at various temperatures and pressures in an autoclave. Two phases were noted in certain ranges. Crystals were grown, using the thermal gradient method.

168. Chumakov, V. D. The Content of Suspended Silicon in Sea Water. *Tr. Sov. Antarkt. Ekspedit. (Leningrad: Morsk. Transport)*, v. 19, 1961, pp. 165-168. Abs. 11G122 in *Ref. Zh., Khim.*, 1962.

Analyses of waters of the southern Pacific show that suspended silica is chiefly concentrated in water of the upper 100-meter layer. A correlation is made with phytoplankton content.

169. Diénert, F., and F. Wandenbulcke. A Study of Colloidal Silica. *Compt. rend.*, v. 178, 1924, pp. 564-566.

Natural waters, examined for silica content by the ammonium molybdate method of analyses, were found to contain noncolloidal silica almost exclusively. This is at variance with the results of Kahlenberg and Lincoln. Neutral or alkaline salts, which are usually present in natural waters, were shown in the laboratory to be effective in converting colloidal silica to noncolloidal silica over time. Conversion was complete in 2 hours at 90° C, in 6 days at 41° C, and 63% complete in 7 days at 37° C. A quartz vessel, which itself is not attacked, seems to have the same effect as the presence of salts.

170. Fokeev, V. M. Physicochemical Properties of Water and Water-Containing Systems. *Izv. Vysshikh Uchebn. Zavedenii, Geol. i Razvedka*, v. 7, No. 5, 1964, pp. 74-82.

The solubility of igneous rocks in water increased with increasing pressure and decreased with increasing temperature. Since most natural waters contain NaCl, a study was made of the H₂O-NaCl system, and curves of the dependence of critical temperature and pressure on NaCl content plotted. In a Na₂O-SiO₂-H₂O system, the SiO₂ in gas phases increased with increasing temperature and pressure.

171. Folk, R. L. The Alteration of Feldspar and Its Products as Studied in the Laboratory. *Am. J. Sci.*, v. 245, 1947, pp. 388-394.

A large amount of research has been done in the laboratory on the alteration of the feldspars and the production of the attendant secondary minerals. This experimental work, covering a period of about 20 years, has been compiled into several phase diagrams which show the influence that acidity, temperature, and the concentrations of aluminum and potassium have on the differential formation of sericite (muscovite), kaolin, and pyrophyllite. The mechanism of formation is also reviewed.

172. Ginzburg, I. I., and E. S. Kabanova. Silica Content and Its Form in Natural Waters. *Kora Vyvetrivaniya, Akad. Nauk SSSR, Inst. Geol. Rudnykh Mestorozhd., Petrogr., Mineralog., i. Geokhim.*, No. 3, 1960, pp. 313-341.

Silica in natural waters can be classified into five categories: (1) ionic and molecular, (2) aggregate, including colloidal and gel, (3) adsorbed, (4) stable, including living organisms and

plankton detritus, and (5) organic (humites). The silica content of meteoric, stagnant, polar, subtropic, marshy, mineral, and H₂SO₄-containing waters is given. Cl⁻ decreases and CO₂ increases the SiO₂ content.

Ca and Mg cause precipitation of SiO₂ if SiO₂ is present in large amounts.

173. Greenberg, S. A., and E. W. Price. The Solubility of Silica in Solutions of Electrolytes. J. Phys. Chem., v. 61, 1957, pp. 1539-41.

The solubility of colloidal silica in solutions of electrolytes and in alkaline solutions was examined. The solubility of silica was explained on the basis of two equilibrium constants: (1) $K = \frac{a_{H_4SiO_4}}{a_{H^+}^4 a_{SiO_4^{4-}}}$ and (2) K_1 the first ionization constant of silicic acid. The pK_1 ($-\log K_1$) values at 25 and 35° were evaluated from solubility and pH measurements and are 9.77 ± 0.05 and 9.70 ± 0.05 , respectively. The concentrations of silicic acid H₄SiO₄ and the silicate ion H₃SiO₄⁻ are not markedly affected by ionic strengths up to 0.1 normal in electrolyte concentration. In solutions with concentrations of salts 1N and above, the solubility decreases.

174. Ingerson, E. Relation of Critical and Supercritical Phenomenon of Solutions to Geological Processes. Econ. Geol., v. 29, 1934, pp. 454-470.

(1) All gases above their critical temperatures can probably carry nonvolatile solids in solution. Water is the most important solvent from the geologic point of view. It has been shown that water above its critical temperature can carry at least 5 percent of its weight of alkali halides and, independent of the alkalis, appreciable amounts of silica.

(2) The critical temperature and critical pressure of such solutions of nonvolatile solutes exceed those of the pure gas by an amount that is proportional to the concentration of the solution.

The presence of other volatile substances may bring about a decrease of the critical temperature.

(3) Gases at supercritical temperatures may dissolve nonvolatile solutes even though the pressure is below their critical pressure. Experimental work is needed in this field.

(4) The fact that gases may carry nonvolatile material in solution proves helpful in explaining some features of

- a. Gaseous transfer of nonvolatile material from magmas.
- b. Pyrometasomatic deposits, as to (1) contained substances (even silica), and (2) depth of formation.
- c. Volcanic "sublimates" of nonvolatile substances.

(5) Undoubtedly much gaseous transfer of material is effected by means of volatile compounds, but gaseous solutions are probably important in certain cases.

(6) The experimental work is quite definite as far as it goes, but very little work has been done on geologically important substances. Therefore, the applications to geology are mere suggestions, because it is impossible to state at present just how far these principles may be applied geologically.

175. Ingri, N. Equilibrium Studies of Polyanions. 4. Silicate Ions in NaCl Medium. *Acta Chem. Scand.*, v. 13, No. 4, 1959, pp. 758-775.

Equilibria in silicate solutions, studied in 0.5 M (molal) NaCl at 25° C, using emf's with a hydrogen electrode, indicate the presence of a polynuclear species containing three or four Si atoms in addition to the presence of the mononuclear Si(OH)_4 , SiO(OH)_3^- , and $\text{SiO}_2\text{(OH)}_2^{--}$. Assuming a single predominating polynuclear species in the range studied, the best agreement was obtained with $\text{Si}_4\text{O}_6\text{(OH)}_6^{--}$. The data, which cover total silica concentrations (B) from 0.0025 to 0.080 M, are given in the form of $Z[\log (\text{OH}^-)_B]$ curves. Equilibrium constants are deduced for silicate reactions at 25° C, 0.5 M NaCl. The possible structures for silicate ions in solution are reviewed, and it is proposed that the present data indicate the predominance of ringlike complexes containing four Si atoms.

176. King, H. M. On the Occurrence of Silica in the Waters of Passamaquoddy Bay Region. *Contrib. Canadian Biol. and Fisheries*, v. 7, Nos. 8-11, Ser. D, Nos. 1-4, 1931, pp. 129-137.

A study of the occurrence of silica in the waters of Passamaquoddy Bay region has shown very little difference in amount from top to bottom in localities where the turning-over of water was very

marked, but where the water movement was not so pronounced, the values varied considerably with depth. The silica content of the water decreased during the summer months. Fresh waters tributary to the bay had a higher silica content than that of the waters of the bay itself.

177. Kissin, I. G., and S. I. Pakhomov. Certain Data on the Role of High Temperatures and Pressures in the Formation of Chemical Composition of Underground Waters. Dokl. Akad. Nauk SSSR, v. 163, No. 1, 1965, pp. 201-204.

One part of samples of aleurites, clays, and limestones was treated with five parts of either distilled water or several chloride-calcium-sodium solutions at 18°-200° C and pressures up to 320 atm for 7 hours. At constant temperature, an increase in pressure from 3 to 209 atm causes an increase in pH, total minerals concentrations, and in Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Cl^- and HCO_3^- concentrations, and a decrease in Mg^{2+} , SO_4^{2-} , BO_3^{3-} , and SiO_2 concentrations.

In general, an increase in temperature caused a decrease in pH and an increase in the total mineral and K^+ , Ca^{2+} , HCO_3^- , and SiO_2 concentrations.

178. Kitahara, S. Solubility Equilibriums and the Rate of Solution of Quartz in Water at High Temperatures and Pressures. Rev. Phys. Chem. Japan, v. 30, 1960, pp. 122-130.

The solubility constant for a solution of quartz in steam was determined. The heat of solution and rate of solution at elevated temperatures were measured. NaCl increases the rate of solution.

179. Kitahara, S. Solubility of Quartz in Aqueous NaCl Solutions at High Temperatures and Pressures. Rev. Phys. Chem. Japan, v. 30, 1960, pp. 115-121.

The solubility of quartz in 1, 3, and 7% NaCl solutions up to 500° C was measured. Above 280° C, the solubility was greater than in water. Above the critical temperature, the effect of the NaCl becomes greater as the density of the solution becomes smaller.

180. Kitahara, S., and F. Osima. Hydrothermal Studies on Silica in Sodium Chloride Solution. Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.), v. 82, 1961, pp. 1436-1441.

Studies were made of the solubility of quartz in water or NaCl solutions at 340°-500° C up to maximum pressures of 900 atm. Colloidal silica slowly formed, accompanied by a decrease of silicic acid of low-molecular weight. After 6 months, a feathery precipitate formed in the NaCl solution. Solubilities of amorphous silica at 25°-100° C are given.

181. Kot, A. A., and Yu. V. Zenkevich. Investigation of the Salts and Silicic Acid-Containing Compounds in the Rotor Part of the Turbine SVK-150 and in the Intermediate Superheaters. Vnutrikotlovye Fiz.-Khim. Protssessy, Akad. Nauk SSSR, Energ. Inst., 1957, pp. 300-310.

Salts and SiO₂ are deposited in turbines when the steam load is suddenly decreased. Salts do not precipitate if they are present in amounts less than 0.02 mg/kg. No silica precipitates on the rotor if less than 0.010-0.015 mg SiO₃⁻⁻⁻ is present in the steam. Increased silica precipitation occurs with increase of silica content. Intermediate cooling of the steam and withdrawal of the condensed water result in purification of the steam.

182. Kot, A. A. The Methods for Conducting Thermochemical Experiments With Cylindric High-Pressure Boilers. Vnutrikotlovye Fiz.-Khim. Protssessy, Akad. Nauk SSSR, Energ. Inst., 1957, pp. 214-226.

Sampling equipment is described which makes possible the removal and analysis in situ of steam samples. Data for the entrainment of SiO₂ and salts are presented.

183. Krasikova, V. M. Solubility and Forms of Occurrence of Silicic Acid in Solutions During Weathering Processes. Inform. Sb., Vses. Nauchn-Issled. Geol. Inst., No. 50, 1961, pp. 95-100. Abs. 16G108 in Ref. Zh., Khim., 1962.

The solubility of the silicic acids H₂SiO₃, H₄SiO₄, H₂Si₂O₅ and H₁₀Si₂O₉ was found to increase with an increase of temperature and a decrease in pH down to a minimum solubility of pH 3. The solubility decreases with an increase of salt concentration. True solutions exist at pH ≤ 9. Silicic acid, present in excess, is in colloidal state. The degree of polymerization increases with increase of acid, temperature, and salt concentration.

184. Krauskopf, K. B. Dissolution and Precipitation of Silica at Low Temperatures. Geochim. et Cosmochim. Acta, v. 10, No. 1/2, 1956, pp. 1-26.

The dissolution of amorphous silica as monosilicic acid and the establishment of solubility equilibrium with silica gel and with colloidal silica have been demonstrated in recent chemical papers. The rates of dissolution and precipitation are slow at ordinary temperatures; at temperatures near the boiling point, both solubilities and rates of dissolution are much higher. The solubility is little affected by pH between values of 1 and 9, but rises rapidly at pH's over 9.

On the basis of this work and supplementary experiments, the geologic literature on the low-temperature solubility of silica is reviewed and various geologic applications are suggested. Much of the confusion in the literature can be traced to failure to recognize the slowness with which silica dissolves and precipitates or polymerizes. Opal dissolves in hot water to about the same extent as other forms of amorphous silica; probably it has a comparable solubility also at lower temperatures, but the rate of dissolution is so extremely slow that massive opal and diatomite can exist almost indefinitely in the presence of natural waters.

In sea water, amorphous silica has about the same solubility as in fresh water. Silica in true solution is not precipitated by electrolytes; colloidal silica may be precipitated by electrolytes, the rate and completeness of precipitation depending on pH and on the kind and concentration of the ions.

Most of the silica in natural waters is in true solution rather than in colloidal dispersion. This means that silica brought to the sea by streams cannot be coagulated by the electrolytes of sea water. The factors that keep the concentration of silica below its equilibrium solubility (with respect to amorphous silica) in most natural waters are not completely understood; the slowness in dissolution, the use of silica by organisms, and slowly established equilibria with crystalline silica or with authigenic silicates doubtless all play a part. The origin of sedimentary chert may be plausibly ascribed to dissolution of remains of siliceous organisms and reprecipitation of the silica (initially as amorphous silica), but not in general to direct inorganic precipitation.

185. Lagerström, G. Equilibrium Studies of Polyanions. Acta Chem. Scand., v. 13, No. 4, 1959, pp. 722-736.

Equilibria in silicate solutions have been studied to 0.5 M (molal) $\text{Na}(\text{ClO}_4)$ medium at 25° and 50° C, and in 3 M $\text{Na}(\text{ClO}_4)$ medium at 25° C, using emf's with a hydrogen electrode, at a

series of total Si concentrations, B. The data are given in the form of curves $Z(\log h)_B$, or $Z(\log [\text{OH}^-])_B$, where h is the concentration of free H^+ and Z is the average number of OH^- bound per $\text{Si}(\text{OH})_4$ in the solution, thus the average negative charge per Si. The data for 0.5 M medium, $Z = 0.70$ to 1.0 , could be explained in terms of the species $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{--}$, and $\text{Si}_4\text{O}_6(\text{OH})_6^{---}$. The data in 3 M medium, $Z = 0.8$ to 1.6 could be explained assuming equilibria between the three mononuclear species mentioned, and, in addition, $\text{Si}_2\text{O}_3(\text{OH})_4^{--}$ and $\text{Si}_4\text{O}_8(\text{OH})_4^{----}$. The equilibrium constants arrived at are given; they are not considered as final. Equilibria are rapidly obtained, and the solutions are clear, as long as no part of the solution is allowed to pass, even momentarily, into the "instability" range, an area in the $(B, \log h)$ field, where a colloid precipitates. This may have been one source of error in earlier work.

186. Li, F. H., Y. T. Wu, L. F. Wang, and C. H. Chen. Physical-Chemical Processes of Silicates in the Estuarial Region. 1. A Preliminary Investigation on the Distribution and Variation of Reactive Silicate Content and the Factors Affecting Them. Hai Yang Yu Hu Chao, v. 6, No. 4, 1946, pp. 311-322.

The reactive silicate content of filtered river water was not changed by mixing it with desilicated sea water or with NaCl , MgCl_2 , or Na_2SO_4 . The reactive silicate content of unfiltered river water decreased gradually when mixed with desilicated sea water. This result supports Bien's belief that suspended matter is necessary for the removal of silicate. Analyses of samples of estuary water at the mouth of the Jiu-Long River indicates a relation between reactive silicate content and chlorinity similar to that reported by Bien. A chemical or physical transformation of silicates occurs upon entrance of river water into the sea. It is probably that adsorption on the surface of suspended or colloidal particles is the first step. It was shown that the rate of adsorption of reactive silicate on colloidal $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ in the laboratory increased with increasing salinity, and adsorption was almost complete.

187. Lovering, T. G., and L. E. Patten. The Effect of CO_2 at Low Temperature and Pressure on Solutions Supersaturated With Silica in the Presence of Limestone and Dolomite. Geochim. et Cosmochim. Acta, v. 26, July 1962, pp. 787-796.

The effect of 1 atm of CO_2 over initially neutral solutions supersaturated with silica, at room temperature, as contrasted with 1 atm of air was determined over a period of 5 months, together

with changes brought about by the introduction of calcite and dolomite to these solutions in the form of either chips or finely ground powder. In the absence of CO_2 , all solutions quickly reached equilibrium and no silica precipitated. In the presence of CO_2 , approximately two-thirds of the silica precipitated as silica gel within the first 2 months; the amount of silica precipitated was not affected by the presence of limestone or dolomite. Silica gel precipitated as a fine powder in the presence of finely ground calcite and dolomite, but as a cloudy gelatinous mass in the presence of coarse chips of dolomite and calcite, and in the absence of either calcite or dolomite. Preferential leaching of calcium from dolomite took place, both in the presence of air and in the presence of CO_2 , but was more pronounced in the presence of air. There was no evidence of physical replacement of either limestone or dolomite by precipitated silica.

188. MacKenzie, F. T., and R. M. Garrels. Silicates: Reactivity With Sea Water. Science, v. 152, No. 3692, October 1965, pp. 57-58.

Silicate minerals rapidly release silica to sea water. Fine-grained, 1-gram samples were placed in 200 milliliters of sea water, and the silica content of the water was measured intermittently for 6 months. At the end of 10 days and of 6 months, the silica concentrations with various minerals, in parts per million, were, respectively: kaolinite, 0.6, 2.2; chlorite, 2.5, 2.4; illite, 1.8, 2.6; muscovite, 1.8, 3.9; montmorillonite A, 7, 10.5; montmorillonite B, 10, 21. Except for ion exchange phenomena, it generally has been assumed that these minerals do not react significantly with sea water, or, if they do, they react at geologically slow rates. The rates observed indicate that the ocean must be looked upon as a chemical system with a rapid response to added detrital silicates.

189. MacKenzie, F. T., R. M. Garrels, O. P. Bricker, and F. Bickley. Silica in Sea Water: Control by Silica Minerals. Science, v. 155, No. 3768, Mar. 17, 1967, pp. 1404-1405.

Silicate minerals typical of those carried in the suspended load of streams release silica to silica-deficient sea water and abstract silica from silica-enriched sea water. Experimental rates of release and uptake permit the conclusion that the suspended solids carried into the oceans by streams are a major factor in the control of the concentration of silica in the ocean.

190. Maéda, H. The Relation Between Chlorinity and Silica Concentration of Water Observed in Some Estuaries. Publ. Seto Marine Biol. Lab., v. 2, No. 2, 1952, pp. 249-255.

Surface, middle, and bottom layer samples of Yosa-nakai and Kojima Bay waters taken at varying distances from the entrance of rivers into the bays were analyzed for chlorinity and silicate content, and a relationship determined expressed by the formula $[\text{SiO}_2] + A[\text{Cl}] = B$. Coefficient A and B showed seasonal or occasional change. High chlorinity is characteristic of sea water; high silicate concentration is indicative of river or stagnant water. Data indicate the degree of mixing of river and sea water.

191. Maéda, H. The Relation Between Chlorinity and Silicate Concentration of Water Observed in Some Estuaries. 2. Norinsho Suisan Koshuskio Kenkyu Hokoku. J. Shimonoseki Coll. Fisheries, v. 3, 1953, pp. 167-180.

(1) Many influence-formulae are shown.

(2) Silicate-chlorine relation can be represented even in surface water by the formula $[\text{Cl}] = \text{constant}$ prevailing in bottom stagnant water, when the water is stagnant and the river can be regarded as being nearly dried up.

(3) The relation between two constants, A and B, is represented by the formula: $B = 807 + 15.9 A$.

(4) All relation formulae pass through the point ($[\text{Cl}] = 15.9$, $[\text{SiO}_2] = 807$) or thereabout.

(5) The difference of the formulae can be represented simply by the difference of the inclination; thus we may be able to make a rough estimation of the influence of a certain river from any one arbitrary sample.

192. Maéda, H., and K. Takesue. The Relation Between Chlorinity and Silicate Concentration of Waters Observed in Some Estuaries. 5. Consideration Upon the Fitness of $[\text{Cl}] - [\text{SiO}_2]$ Relation of the River Water for the Relation Formula Computed From the Estuarine Waters and Upon the Seasonal Variation of the Estimated Contents. Records Oceanog. Works Japan, v. 6, 1961, pp. 112-119.

The relation between the Cl^- and SiO_2 of both the Yorimo River and of its estuary waters can be expressed by $A[\text{Cl}] + [\text{SiO}_2] = B$, where A and B are constants subject to seasonal variation, and $B = 0.755 + 17.07 A$.

193. Makimoto, H., H. Maéda, and S. Era. The Relation Between Chlorinity and Silicate Concentration of Water Observed in Some Estuaries. 3. Records Oceanog. Works Japan, v. 2, No. 2, March 1955, pp. 106-112.

Surface and bottom-layer samples of Ariakne sea waters taken near the point of entrance of the Chikugo River into the estuary were analyzed for chlorinity and silicate content and a relationship determined expressed by the formula $[\text{SiO}_2] + A[\text{Cl}] = B$. New values were found for relation of A to B: $B = 0.0037 + 17.665 A$. Results indicate the degree of mixing of river and sea water.

194. Matsumori, M., T. Nishijima, and H. Nakayama. Experimental High-Pressure Boiler. Netsu-Kanri, v. 11, No. 20, 1959, pp. 26-31.

SiO_2 , but not Cl^- , was carried over in boiler water at 100-200 kg/cm^2 , and at pH 9.0. The addition of Na_2SO_4 to remove O is not recommended, because it decomposes under these conditions.

195. McKeague, J. A. Silica in Solution in the Presence of Soil and Related Material: Forms, Concentrations, and Reactions. Ph.D. Thesis, Cornell Univ., Ithaca, N.Y.; University Microfilms, Ann Arbor, Mich., 1962, 186 pp.

In a series of experiments on the solubility of silica in the presence of soil, silica in the aqueous phase was shown by a simple chemical test to be in the form of $\text{Si}(\text{OH})_4$, and not silica sol. The dissolution of silica from soil material by aqueous solutions was found to decrease with increasing pH in the range of pH 4.5 to pH 9, to increase approximately linearly with increase in temperature within the range from 4°C to 43°C , and to increase with an increase of soil-water ratio. An initially rapid rate of dissolution was followed in all cases by a slower rate. These results support the hypothesis that the dissolution of silica from soil involves a desorption of adsorbed silica.

Another series of experiments indicated that the removal of $\text{Si}(\text{OH})_4$ from aqueous solutions by the addition of known weights of soil components was an adsorption reaction, because it depended on the surface area of any one added solid, and approximately followed Freundlich's adsorption isotherm. The reaction was also pH dependent. Adsorption increased within a range from pH 4 to pH 9. Precipitated hydroxides of polyvalent metals were very effective in removing monosilicic acid from solution; ground bauxite and a highly ferruginous soil much less so; and gibbsite and calcite not at all.

196. McKeague, J. A., and M. G. Cline. Si in Soil Solutions. 1. The Form and Concentration of Dissolved Si in Aqueous Extracts of Some Soils. Canadian J. Soil Sci., v. 43, No. 1, 1963, pp. 70-82.

The effects of soil-H₂O ratio, pH, method of equilibration, time, and temperature on the form and concentration of dissolved Si in soil-H₂O mixtures were studied. Borate buffer solutions showed an inverse relation between pH and Si content. Temperature increase caused an increase of 0.2 ppm of SiO₂ per degree. Salt concentrations of 0.01 and 0.001 M NaCl, CaCl₂, BaCl₂, and MgSO₄ did not effect Si solubility. NaHCO₃ lowered solubility.

197. Morey, G. W. The Solubility of Solids in Gases. Econ. Geol., v. 52, No. 3, May 1957, pp. 225-251.

That gases can dissolve solids has been known since the work of Hannay in 1879-1881. The historical and theoretical aspects of this phenomenon are discussed, and the literature of the subject is summarized. The solubilities of NaCl, KCl, and SiO₂ in steam are reviewed. New data on the solubility of UO₂, Al₂O₃, NiO, Nb₂O₅, Ta₂O₅, BeO, and GeO₂ at 500° C, 1,000 bars steam pressure, are included.

198. Natarov, V. D., and D. I. Betin. Study of the Solubility of the Chief Minerals of the Krivoi Rog Rock Series. Sb. Nauchn. Statei Nauchn.-Issled. Gornorudn. Inst. Ukr. SSR, No. 9, 1962, pp. 167-171; Abs. 2V359 in Ref. Zh., Geol., 1963.

A series of experiments were conducted to determine the possible conditions of formation of Fe ore deposits. The solubility of the ore and the gangue minerals in water of varying mineral content and composition at 20° and 1-200 atm (conditions similar to supergene) was studied. Average solubility values of SiO₂, Al₂O₃, and Fe are 10-11, 5-6, and 0.3-1.0 mg/l, respectively. The highest solubility of SiO₂ is in an alkali medium (24 mg/l) and in CaCl₂ solutions (sometimes to 44 mg/l); the solubility of SiO₂ is considerably less in NaCl, Na₂SO₄, and distilled H₂O. Even when SiO₂ solubility is low, it is related to pH (the coefficient of correlation is positive) and has an inverse relation to mineral content. Fe solubility has a high negative relation with pH and a positive relation with mineral content. A statistical treatment of 371 chemical analyses of shaft waters gave similar results. The solubility of minerals was studied in solutions of varying mineral content and composition at 150°-500° C and 300-900 atm. Under these conditions, SiO₂ solubility is 50-100 times that at low temperature, reaching in some cases 1,500-2,000 mg/l. Fe solubility, in most cases, is 2-3 times

and only sometimes 100 times as much, reaching 200 mg/l. A 1° increase in the temperature of the solution increases SiO₂ solubility by 0.8-4.0 and Fe solubility by 0.02-1.0 mg/l. A 1-atm increase in pressure increases the solubility of SiO₂ and Fe by 0.05-0.4 and 0.02-0.1 mg/l, respectively. A 1-unit increase in pH decreases solubility of SiO₂ and Fe by 20-130 and 0.2-6.0 mg/l. Conditions of the formation of the Krivoi Rog Fe ore deposits were examined from the point of view of these data.

199. Ostrowski, S. Silicon Content of the Gdansk Bay Waters. *Acta Geophys. Polon.*, v. 10, No. 2, 1962, pp. 165-171.

Salinity and Si measurements were made on Gdansk Bay samples. The effect of season of the year, depth, currents, meteorological conditions, and distance from the Vistula River estuary were determined. Si content is a better indicator of fresh water influx than is salinity content.

200. Richards, F. A. Dissolved Silicate and Related Properties of Some Western North Atlantic and Caribbean Waters. *J. Marine Res.*, v. 17, 1958, pp. 449-465.

Dissolved silicate, phosphate, oxygen, salinity, and temperature were measured in surface, intermediate, and deep waters of various regions of the Western North Atlantic Ocean and Caribbean Sea, and relationship between the factors established. In surface waters, where silicate is low, its ratio to phosphate, nitrate and O consumption is variable. In intermediate depths, silicate, phosphate, and nitrate regeneration and O consumption proceed in definite atom ratios. Silicate is linearly related to biological processes. In deep water, the silicate/phosphate ratio increases.

201. Rozanov, A. G. Distribution of Phosphates and Silicates in Water of the Northern Part of the Indian Ocean. *Tr. Inst. Okeanol. Akad. Nauk SSSR*, v. 64, 1964, pp. 102-114.

The soluble SiO₂ concentration increases to a maximum of 5, 20, and 160 Y/liter in the surface, thermocline, and bottom layers, respectively. The organic P content is 0.0-0.27, 0.18-0.51, and 0.06-0.19 Y/liter in the surface, thermocline, and deeper layers; the total PO₄ is 0.1-0.4, 2.3-2.9, and 2.3-2.4, respectively.

202. Siever, R. Silica Solubility, 0°-200° C, and the Diagenesis of Siliceous Sediments. *J. Geol.*, v. 70, No. 2, March 1962, pp. 127-150.

The data on solubility of amorphous silica and quartz at low temperatures are reviewed. Determinations of the metastable equilibrium solubility of amorphous silica at 25° C in distilled water and artificial sea water give values of about 140 ppm, in agreement with earlier workers' results. Solubility in simulated oilfield brines of 3% to 5% dissolved salts concentrations is about the same. Solubility was drastically reduced in peat waters, presumably due to adsorption of organic material on free silica surfaces. Quartz solubility was determined between 125° and 181° C in sealed bombs; the results interpolate well between the lower temperature data of Van Lier and the higher temperature data of Kennedy. The solubility of quartz under directed stress at 95° C approximates that of amorphous silica at the same temperature.

Diagenetic changes in silica content of sediments, in particular the origin of chert and silica cementation of sandstones, are explained by the metastability of amorphous silica, the dissolution of biogenic amorphous silica, the effects of increased ionic strength of subsurface formation waters on silica and carbonate solubility, the equilibria between clay minerals of differing Si/Al ratios, the action of clays as semipermeable membranes, and the effects of pressure and temperature increase on burial.

203. Sillén, L. G. The Physical Chemistry of Sea Water. Ch. in Oceanography, Proc. Internat. Oceanographic Cong., ed. by Mary Sears. American Association Advancement Science, Washington, D. C., 1961, pp. 549-581.

A comparison is made between sea water and an imaginary model to be made by introducing in succession the following ingredients: H₂O and SiO₂; Al(OH)₃; HCl, NaOH, KOH, MgO and CaO; CaCO₃ and MgCO₃; O₂; FeO and FeOOH; TiO₂; HF; H₂SO₄; H₃PO₄, or Na₂HPO₄; MnO₂. In the model, most of the phases will be to an appreciable degree solid solutions. Complex formation, some anion oxidation-reduction equilibria, and some possible solubility equilibria of Sr and Ba, Co, Ni, Cu, Pb, and Au are considered.

204. Sugihara, T. Chemical Researches on the Hot Springs of Misasa, Tottori Prefecture. 5. Variation of Silica Content. Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.), v. 81, 1960, pp. 703-710.

Correlations were made between the SiO₂ content of 30 springs over a 12-month period and the temperature, Cl⁻, Mg, Fe, Rn, and pH. There is a positive correlation of SiO₂ with Cl⁻. The SiO₂/Cl⁻

ratio decreases with increasing Cl^- concentration. The concentration of ionic SiO_2 changes during the first 5 hours after collection, then becomes stable.

205. Syromyatnikov, F. V. Experimental Data on the Solubility of Minerals, and Genetic Conclusions. Cong. Geol. Internat., Compt. Rend., 20th sess., Mexico City, Mexico, Sec., 11-A, 1956, (pub. 1959), pp. 321-346.

Quartz, halite, galena, and cassiterite were found to be congruently soluble in measurements made in an exclave at 200° - $1,000^\circ$ C and 300-2,000 kg/sq cm. Calcite, pyrite, and albite were found to be incongruently soluble.

206. Vlasov, N. A., and E. A. Morgen. The State of Silicic Acid in Aqueous Solutions. Izv. Fiz.-Khim. Nauchn.-Issled. Inst. Irkutskom Gosudarst. Univ., v. 6, No. 1, 1964, pp. 192-199. Abs. 3B715 in Ref. Zh., Khim., 1965.

Molecularly dispersed (ionic) silicic acid is determined colorimetrically by the yellow molybdosilicate complex. The difference between this value and the value for total silica represents polymerized silicic acid. In NaOH solutions, ionic and low-molecular-weight silicic acid exists. The degree of polymerization increases at lower pH values. Polymerization of silicic acid increases with increase of NaCl concentration up to a NaCl concentration of 3 mg/ml.

207. Wannesson, J. Geochemical Properties of Silica. Compt. rend., v. 256, No. 13, March 1963, pp. 2888-2890.

The effect of the presence of CaCO_3 , CaSO_4 , FeCl_3 , or $(\text{NH}_4)_2\text{S}$ on the amount of silica dissolved from sand and from various types of clays was determined. pH was of secondary importance. The silica content of waters from petroliferous beds is much greater than that of quartz, but less than that of amorphous silica. Such water can either dissolve amorphous silica or deposit quartz, depending on conditions. Water from calcareous reservoirs contains as much silica as does water from siliceous reservoirs.

208. Wey, R., and B. Stiffert. Reaction of Monomolecular Silica in Solution with Al^{+++} and Mg^{++} . Colloq. Internat. Centre Natl. Rech. Sci. (Paris), No. 105, 1962, pp. 11-23.

The solubility of silica is dependent upon pH, temperature, and form of aggregation. It is independent of the presence of Na^+ ,

Cl^- , SO^{--} , and Ca^{++} ions. Al^{+++} and Mg^{++} cause precipitation at certain pH values, with Mg^{++} forming crystallized materials of the clay type. The presence of a second solid phase does not affect solubility, because monomolecular silica is not adsorbed by clays or by hydroxides.

209. Zenkevich, Yu. V., and B. G. Dement'ev. The Influence of the Time of Contact on the Solubility of Some Compounds in Water Vapor. Teploenerg., v. 10, No. 8, 1963, pp. 50-54.

The solubility of NaCl, quartz, and Na_3PO_4 in superheated H_2O vapor was determined at $355^\circ\text{-}400^\circ\text{C}$, 76-95 atm, and vapor-flow rates of 30-70 kg/hr. An increase in vapor-flow results in lower NaCl concentration. Below 400°C , the presence of NaCl lowers the solubility of SiO_2 ; the presence of SiO_2 increases the solubility of NaCl.

CORROSION PREVENTION

Solutions containing alkali silicates are used to coat metals with amorphous silica to retard corrosion. The silicate adsorbs to the metal, forming a protective film.

Selected References

210. Harbaugh, R. L. (assigned to Inland Steel Co.). Coatings for Corrosion Protection of Zinc and Aluminum-Surfaced Articles. U.S. Pat. 2,989,418, June 20, 1961.

Zn or Al surfaces are protected against corrosion by deposition of a silica gel coating, formed by reaction between an alkali metal silicate and chromic acid.

211. Johnson, C. E., and L. E. Hummel (assigned to Nalco Chemical Co.). Corrosion-Inhibiting Compositions, Especially for Cooling Solutions. U.S. Pat. 2,972,581, Feb. 21, 1961.

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212. Lehrman, L., and H. L. Shuldener. The Role of Sodium Silicate in Inhibiting Corrosion by Film Formation on Water Piping. J. Am. Water Works Assoc., v. 43, No. 3, March 1951, pp. 175-188.

Solutions of different sodium silicates in very low concentration (12-1,400 ppm SiO_2) are shown to achieve an equilibrium between ionic and colloidal silica, the rate being slower as the concentration increases. Silica is not removed from these solutions by metals until the solid corrosion products of the metals form. The siliceous film which forms on the corroding metals and inhibits the corrosion process is identified by chemical analysis, microscopic examination and X-ray diffraction pattern as being predominantly amorphous silica. The mechanism of removal of silica from very dilute solutions of sodium silicate by zinc hydroxide is shown to be adsorption (chemisorption), resulting in the formation of an adsorption compound.

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Treatment of acid drinking water with $\text{Na}_2\text{O}:2\text{SiO}_2$ and of more alkaline water with $\text{Na}_2\text{O}:3.25\text{SiO}_2$ at two water-treating plants was found to reduce corrosion of iron pipes. The mechanism of the protective action is discussed, as well as the method of feeding the silicate, the physiological action of silicates, and the method of determining silica.

AUTHOR INDEX

<u>Name</u>	<u>Item No.</u>
A	
Akabori, H.	5
Akahane, M.	65, 72
Alexander, G. B.. . . .	105, 106
Anderson, G. M.	107
Aoki, F.. . . .	1
Arino, H.	131
Atkins, W. R. G.. . . .	164, 165
Aver'yanova, L. N.. . . .	73
B	
Bangham, D. H.. . . .	13
Barrer, R. M.	31, 32, 33, 34, 66
Bartholomé, P.. . . .	166
Bassett, H.	74
Baumann, H.	108
Beckwith, R. S.	109
Berman, H.. . . .	2
Betin, D. I.. . . .	198
Bickley, F.	189
Bien, G. S.	75
Bogomolov, G. V.. . . .	21
Bowen, N. L.. . . .	60
Brannock, W. W.	63
Bricker, O. P.. . . .	189
Brindley, G. W.	36
Bunchuk, L. V.. . . .	50
Burke, O. W., Jr.	76
Burnham, C. W.. . . .	107
Butuzov, V. P.. . . .	167
C	
Chang, T. N.. . . .	118
Chen, C. H.	186
Chen, W. T.	146
Chumakov, V. D.	168
Clark, R. H.. . . .	35
Cline, M. G.. . . .	196
Contois, D. E.. . . .	75
Cox, J. E., Jr.	110-111

NameItem No.

D

Dapples, E. C.	22
Datar, D. S.	95
De Kimpe, C.	36, 38
Delgado, M.	44
Dement'ev, B. G.	77, 209
Diénert, F.	3, 169
Dittmann, J.	67
Durov, S. A.	78

E

Era, S.	193
Ervin, G., Jr.	154

F

Filatov, K. V.	79
Flaschen, S. S.	37
Fokeev, V. M.	170
Folk, R. L.	171
Fournier, R. O.	147, 148, 149
Franck, H.	14
Frankel, J. J.	80
Frederickson, A. F.	110, 111
Fresenius, W.	4
Friedman, I.	112
Friedman, I. I.	160
Fron del, C.	113
Fyfe, W. S.	35, 163

G

Ganeev, I. G.	114
Garrels, R. M.	16, 17, 18, 188, 189
Gastuche, M. C.	36, 38, 81
Gillingham, T. E.	39
Ginzburg, I. I.	172
Glemser, O.	62
Goto, K.	82, 94, 115, 116
Gray, J. A.	83
Greenberg, S. A.	117, 118, 173
Grimm, W. D.	84
Gruner, J. W.	68

NameItem No.

H

Harbaugh, R. L.	210
Harder, H.	85
Harman, R. W.	119, 120, 121, 122, 123, 124, 125, 126
Hart, J. S.	86
Hatch, R. A.	40
Heard, H. C.	139
Heitmann, H. G.	87, 127
Hemley, J. J.	41, 69, 147
Hénin, S.	42, 43
Hesselgesser, J. M.	150
Heston, W. M.	106
Hinz, W.	88
Hitchen, C. S.	128, 129
Holt, P. F.	130
Hoyas de Castro, A.	44
Hummel, L. E.	211

I

Iler, R. K.	106
Ingamells, C. O.	12
Ingerson, E.	49, 174
Ingri, N.	175
Ireland, H. A.	23
Iwao, S.	5
Iwasaki, I.	6, 7, 131

J

Jackson, C. B.	76
Jephcott, C. M.	132
Johnson, C. E.	211
Johnston, J. H.	132

NameItem No.

K

Kabanova, E. S.	172
Kahlenberg, L.	133
Kane, J. C.	134
Kanie, T.	8
Kartvelishvili, G. Ya	136
Katsura, T.	7, 131
Keller, W. D.	24, 25
Kelley, K. K.	29
Kennedy, G. C.	137, 138, 139
Kent, L. E.	80
Kikuno, K.	156
King, D. T.	130
King, H. M.	176
Kissin, I. G.	177
Kitahara, S.	140, 141, 178, 179, 180
Kohle, H.	89
Koizumi, M.	5
Koltermann, M.	45
Konstant, Z. A.	61
Kot, A. A.	90, 135, 181, 182
Krasikova, V. M.	183
Krauskopf, K. B.	142, 184
Kuhnert, W. A.	91
Kunth, P. O.	88

L

Lagerström, G.	185
La Mer, V. K.	134
Lehrman, L.	212
Lenher, V.	143
Li, F. H.	186
Lincoln, A. T.	133
Linford, H. B.	134
Loughman, F. C.	26
Lovering, T. G.	187
Lovering, T. S.	92
Luth, W. C.	46, 47
Lyon, S. R.	144

NameItem No.

M

MacKenzie, F. T.	17, 18, 188, 189
Maéda, H.	190, 191, 192, 193
Makimoto, H.	193
Matsumori, M.	194
Mattson, S.	27
Maynard, J. E.	93
McKeague, J. A.	195, 196
Merbaul, N.	213
Merenkov, B. Ya.	48
Merrill, H. B.	143
Millot, G.	145
Minato, H.	5
Moore, E. S.	93
Morey, G. W.	49, 146, 147, 148, 149, 150, 197
Morgen, E. A.	206
Mosebach, R.	151, 152
Mueller, P.	153
Mullin, J. B.	9
Murata, K. J.	63

N

Nachtigall, E.	214
Nakayama, H.	194
Natarov, V. D.	198
Newton, R. C.	139
Ni, L. P.	50
Nishijima, T.	194
Nix, J.	51
Noguchi, K.	51

O

Okamoto, G.	94
Okura, T.	94
Olsen, E.	52
O'Neill, T. F.	70
Osborn, E. F.	37, 55, 56, 57
Osima, F.	180
Ostrowski, S.	199

NameItem No.

P

Pakhomov, S. I.	177
Patten, L. E.	187
Pearce, D. W.	157
Pistorius, C. W. F. T.	53
Plotnikova, G. N.	21
Posnikov, N. F.	78
Price, E. W.	173
Pshemenskii, A. A.	135

R

Rao, A. V. R.	95
Rees, O. W.	10
Reeve, R.	109
Richards, F. A.	200
Riley, J. P.	9
Robichet, O.	42, 43
Roller, P. S.	154
Rowe, J. J.	147, 148, 149
Roy, C. J.	155
Roy, D. M.	54
Roy, R.	54, 55, 56, 57
Rozanov, A. G.	201

S

Samuel, T.	96
Sand, L. B.	57
Sanders, J. E.	28
Saprykina, N. V.	104
Schink, D. R.	11
Schloemer, I. H.	71
Schneider, W.	4
Schrichard, M.	14
Schumann, E.	97
Schwartz, M. C.	98, 99
Sharp, W. E.	100
Shimada, K.	156
Shuldener, H. L.	212
Sidorenko, G. A.	104
Siever, R.	101, 202
Sillén, L. G.	203
Slavnyi, Yu A.	102
Sprauer, S. W.	157

NameItem No.

S

Steinour, H.	158
Stericker, W.	215
Stiffert, B.	208
Stöber, W.	159
Stringham, B.	58
Stumm, W.	19, 20
Styrikovich, M. A.	103
Sugihara, T.	204
Suhr, N. H.	12
Swinchatt, J. P.	28
Syromyatnikov, F. V.	205

T

Takesue, K.	192
Tarutani, T.	7, 131
Taylor, H. F. W.	59
Thomas, W. H.	75
Titova, E. A.	21
Tourky, A. R.	13
Tuttle, O. F.	47, 60, 160

U

Upite, A.	61
Uytterhoeven, J.	81

V

Vaivads, A.	61
Van Nieuwenberg, C. J.	161
Van Zon, P. M.	161
Vlasov, N. A.	206
Vorob'eva, E. S.	102

W

Wandenbulcke, F.	2, 169
Wang, L. F.	186
Wannesson, J.	207

NameItem No.

W

Wasserburg, G. J.	139
Wawrik, F.	162
Weber, W. J., Jr.	19, 20
Weill, D. F.	163
Weitz, E.	14
Weller, W. W.	29
Wendlandt, H. G.	62
Wey, R.	208
White, D. E.	63
White, E. A. D.	34, 66
Wilson, R. C. L.	30
Wu, Y. T.	186
Wyart, J.	64

Y

Yakovleva, M. N.	104
Yano, H.	65, 72

Z

Zaheer, S. H.	95
Zenkevich, Yu V.	77, 181, 209
Zolotukhina, M. D.	15

TITLE INDEX

<u>Title</u>	<u>Index No.</u>
A	
Action of Hot Water on Some Feldspars	146
Addition of Sea Water During Precipitation of Silica Pigment. . .	76
Alkali Feldspar Solvus in the System $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. . .	47
Alteration of Feldspar and Its Products as Studied in the Laboratory.	171
Aqueous Solution of Sodium Silicates. 1. Preparation and Electrical Conductivity	119
Aqueous Solutions of Sodium Silicates. 2. Transport Numbers . .	120
Aqueous Solutions of Sodium Silicates. 3. Sodium Ion Activity .	121
Aqueous Solutions of Sodium Silicates. 4. Hydrolysis.	122
Aqueous Solutions of Sodium Silicates. 5. Osmotic Activity, Lowering of Vapor Pressures and Freezing Points	123
Aqueous Solutions of Sodium Silicates. 6. Heterogeneous Equilibria System: $\text{Na}_2\text{O}:\text{SiO}_2:\text{H}_2\text{O}$ at 25°	124
Aqueous Solutions of Sodium Silicates. 7. Silicate Ions. Electrometric Titrations: Diffusion: Colorimetric Estimation. .	125
Aqueous Solutions of Sodium Silicates. 8. General Summary and Theory of Constitution. Sodium Silicates as Colloidal Elec- trolytes.	126
Argillation and Direct Bauxitization in Terms of Concentrations of Hydrogen and Metal Cations at Surface of Hydrolyzing Aluminum Silicates.	25
Artificial Quartz	167
B	
Behavior of Silica in Diagenesis.	22
Boiler Water Treatment: A Formula for the Control of Sludge and Scale in Internal (Carbonate) Treatment	83
Bonding Energies of Some Silicate Minerals.	24
Buffer Systems of Natural Fresh Waters.	19
C	
Chemical Analyses of Some Components in Natural Water	6
Chemical Mass Balance Between Rivers and Oceans	17
Chemical Researches on the Hot Springs of Misasa, Tottori Prefecture. 5. Variation of Silica Content.	204
Coatings for Corrosion Protection of Zinc and Aluminum- Surfaced Articles	210
Colloidal Silica in Natural Waters and the Silicomolybdate Colour Test	13

TitleItem No.

C

Colorimetric Determination of Silica in Natural Waters. 2. . . .	1
Considerations in the Weathering of the Silicate Minerals	26
Constitution and Classification of the Natural Silicates.	2
Content of Suspended Silicon in Sea Water	168
Coprecipitability of Aluminum and Silicic Acid in the System Al ₂ O ₃ -Na ₂ O-SiO ₂ -H ₂ O With Change in pH (In Connection With the Problem of the Origin of Bauxite)	104
Correlations of the Surface Properties of Silica and Its Behavior in Natural Media	81
Corrosion Behavior of Highest-Purity Aluminum	214
Corrosion-Inhibiting Compositions, Especially for Cooling Solutions	211
Critical Problems in the Boiler Feedwater Field	98

D

Data on the Role of High Temperatures and Pressures in the Formation of Chemical Composition of Underground Waters	177
Deep-Sea Origin of Radiolarian Cherts	28
Deposition of Hydrothermal Quartz and Calcite	100
Deposition of Sodium Chloride and Silica in Turbine Indicators. .	77
Determination of Silica in High-Purity Water by an Ion-Exchange Method.	8
Determination of Silica in Sea Water Using Solvent Extraction . .	11
Determination of Silica in Waters	3
Determination of Silicic Acid in Mineral Waters	4
Determination of Small Amounts of Silicic Acid in Aqueous Solutions	15
Dissolution and Precipitation of Silica at Low Temperatures . . .	184
Dissolved Silicate and Related Properties of Some Western North Atlantic and Caribbean Waters	200
Distribution of Phosphates and Silicates in Water of the Northern Part of the Indian Ocean	201

E

Effect of CO ₂ at Low Temperature and Pressure on Solutions Supersaturated With Silica in the Presence of Limestone and Dolomite.	187
Effect of Dissolved SiO ₂ on the Conditions of Dolomite Formation	166
Effect of Particle Size on the Solubility of Amorphous Silica in Water.	105

TitleItem No.

E

Effect of pH on Polymerization of Silicic Acid.	115
Effect of Solid Content on the Adsorption and Flocculation Behavior of Silica Suspensions.	134
Effect of Some Inorganic Anions on the Corrosion of Aluminum in Ammonia Water.	213
Effect of Thermal Treatment on the Serpentine of Barranco de San Juan.	44
Electron Micrograph of Some Silica Rocks, With Special Reference to the Micropores With Fluid Inclusions	5
Equilibria in the Systems $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 25° C.	157
Equilibrium Calculations in the System Mg, Fe, Si, O, H, and Ni .	52
Equilibrium Studies of Polyanions	185
Equilibrium Studies of Polyanions. 4. Silicate Ions in NaCl Medium.	175
Experimental Data on the Solubility of Minerals, and Genetic Conclusions	205
Experimental High-Pressure Boiler	194
Experiments on the Synthetic Metasomatism of Magnesium Silicates	67

F

Factors Concerning the Growth of Crystalline Silicates.	31
Feed-Water Problems in Boilers of Low- and Medium-Pressure Stages.	89
Field Measurements of Silica in Water from Hot Springs and Geysers in Yellowstone National Park.	147
Fields of Formation of Some Common Hydrothermal-Alteration Minerals.	58
Formation of Chemical Composition of Ground Waters in the Middle Amur Area and Separation of the Silicate Waters in Classifica- tion of Natural Waters.	79

G

Genesis of Chrysotile Asbestos.	48
Geochemical Properties of Silica.	207
Geochemical Studies of Some Geysers in Yellowstone National Park.	51
Geochemistry of Silica in Sedimentary Environments.	142
Grahamstown Surface Quartzites (Silcretes).	80

TitleItem No.

H

Hydrolysis of K-Feldspar and Mica at Elevated Temperatures and Pressures	69
Hydrothermal Alteration of Feldspars at 250° C. to 400° C.	70
Hydrothermal Alteration of Feldspars in Acid Solutions Between 300° and 400° C.	68
Hydrothermal Chemistry of Silicates. Part 1. Synthetic Lithium Aluminosilicates.	34
Hydrothermal Chemistry of Silicates. Part 2. Synthetic Crystalline Sodium Aluminosilicates	66
Hydrochemical Features of the Chorchán Area Talc Deposit.	136
Hydrothermal Reactions Involving Thallium	59
Hydrothermal Solubility of Quartz as a Heterogeneous Gas Equilibrium	151
Hydrothermal Solubility of Silica	137
Hydrothermal Studies on Silica in Sodium Chloride Solution.	180
Hydrothermal Synthesis of Minerals.	64
Hydrothermal-Synthetic Investigations in Alpine Serpentinities in Connection With an Observed Paragenesis of Minerals.	153
Hydrothermal, Synthetic, Simultaneous Crystallization of Orthoclase and Quartz	71
Hydrous Magnesium Silicates. 3. Synthesis of Magnesium Hydroxilicates From Magnesium Hydroxide Dehydrated at 400° and Silicic Acid.	61

I

Immiscibility in the System $H_2O-Na_2O-SiO_2$	112
Influence of the Time of Contact on the Solubility of Some Compounds in Water Vapor.	209
Interactions in the System $Na_2O-Al_2O_3-SiO_2-CaO-H_2O$ Under the Conditions of Hydrochemical Processes and at Varying Ratios of $CaO:SiO_2$	50
Investigation of the Colloidal Hydrated Calcium Silicates. 2. Solubility Relationships in the Calcium Oxide-Silica-Water System at 25°	118
Investigations in the Systems SiO_2-H_2O and $Co-SiO_2$	144
Ionic Coordination in Alumino-Silicic Gels in Relation to Clay-Mineral Formation.	36

TitleItem No.

L

Laws of Soil Colloidal Behavior. 9. Amphoteric Reactions and Isoelectric Weathering.	27
Leaching of Iron Protores: Solution and Precipitation of Silica in Cold Waters	92
Liquid Immiscibility in the System $H_2O-Na_2O-SiO_2$	160
Low-Temperature Heat Capacities and Entropies at $298.15^\circ K$ of Crystalline Silicates of Barium and Strontium	29

M

Magnesium Silicates at High Temperatures.	45
Mechanism of Hydrogen Ion Buffering in Natural Waters	20
Mechanism of "Solution" of Quartz in Pure Water at Elevated Temperatures and Pressures.	110
Method for the Experimental Investigation of Hydrothermal Solutions, With Notes on Its Application to the Solubility of Silica	128
Methods for Conducting Thermochemical Experiments With Cylindric High-Pressure Boilers	182
Mineralogical Equilibria in the System $K_2O-Al_2O_3-SiO_2-H_2O$	41

O

Occurrence of Silica in the Waters of Passamaquoddy Bay Region. .	176
Occurrence of Silicates in Natural Waters	10
Origin of Granite in the Light of Experimental Studies in the System $NaAlSi_3O_8-KAlSi_3O_8-SiO_2-H_2O$	60

P

Permissible Silicic Acid Content of Medium-Pressure Boilers . . .	97
Phase Equilibrium in the System: $Li_2O-Al_2O_3-SiO_2$	40
Phase Relations in the System $MgO-SiO_2-H_2O$ to High Pressures and Temperatures.	53
Physical-Chemical Processes of Silicates in the Estuarial Region. 1. A Preliminary Investigation on the Distribution and Variation of Reactive Silicate Content and the Factors Affecting Them.	186
Physical Chemistry of Sea Water.	203
Physicochemical Properties of Water and Water-Containing Systems.	170

TitleItem No.

P

Pneumatolytic and Hydrothermal Alteration and Synthesis of Silicates	49
Polymerization of Silicic Acid Obtained by the Hydrothermal Treatment of Quartz and the Solubility of Amorphous Silica. . .	140
Portion of the System Silica-Water.	138
Possible Form of the Transport of Silica in Hydrothermal Solutions	114
Precipitates of Magnesium Salt and Water Glass Solutions. . . .	88
Precipitation of Silica in Sediments Affected by Salines. . . .	84
Precipitation of Silica From Soil Solutions at Freezing	102
Precipitation of Silica in the Presence of Aluminum	82
Precipitation of Silicic Acid	85
Preparation of Synthetic Quartz	32
Properties of Silica in Water	94

Q

Quality of the Steam and the Water Regime in Cylindrical Boilers at High Pressures	90
--	----

R

Reaction of Monomolecular Silica in Solution with Al^{+++} and Mg^{++} . .	208
Reaction of Oxides with Water at High Pressures and Temperatures. .	62
Reactions of Aqueous SiO_2 - $NaOH$ - $CaCl_2$ Systems at $200^\circ C$	65
Relation Between Chlorinity and Silica Concentration of Water Observed in Some Estuaries.	190
Relation Between Chlorinity and Silicate Concentration of Water Observed in Some Estuaries. 2.	191
Relation Between Chlorinity and Silicate Concentration of Waters Observed in Some Estuaries. 5. Consideration Upon the Fitness of $[Cl]$ - $[SiO_2]$ Relation of the River Water for the Relation Formula Computed From the Estuarine Waters and Upon the Seasonal Variation of the Estimated Contents.	192
Relation Between Chlorinity and Silicate Concentration of Water Observed in Some Estuaries. 3.	193
Relation of Critical and Supercritical Phenomenon of Solutions to Geological Processes	174
Removal of Silica From Uranium Leach Solutions.	86
Removal of Silica From Water for Boiler Feed Purposes. The Ferric Sulphate and Hydrous Ferric Oxide Process.	99
Removal of Silicic Acid From New Steam Generators	96

2

TitleItem No.

R

Removal of Soluble Silica From Fresh Water Entering the Sea . . .	75
Removing Dissolved Silica From Alkaline Brines.	91
Results Concerning the Preparation of Argillaceous Minerals in the Laboratory; Synthesis of Autigorite	42
Role of Silica in the Buffering of Natural Waters	16
Role of Sodium Silicate in Inhibiting Corrosion by Film Formation on Water Piping	212

S

Salts and Silicic Acid-Containing Compounds in the Rotor Part of the Turbine SVK-150 and in the Intermediate Superheaters . .	181
Seasonal Charges of the Silica Content of Natural Waters in Relation to Phytoplankton	164
Seasonal Variations in the Phosphate and Silicate Content of Sea Water During 1926 and 1927 in Relation to the Phyto- plankton Crop	165
Semiquantitative Measurements of the Solubility of Quartz in Supercritical Steam	161
Si in Soil Solutions. 1. The Form and Concentration of Dis- solved Si in Aqueous Extracts of Some Soils	196
Silica-Bicarbonate Balance in the Ocean and Early Diagenesis. . .	18
Silica Budget in the Sedimentary Cycle.	101
Silica Content and Its Form in Natural Waters	172
Silica Content of Natural Waters.	7
Silica Diagenesis in Upper Jurassic Limestones of Southern England	30
Silica in Hot-Spring Waters	63
Silica in Natural Waters.	155
Silica in Sea Water: Control by Silica Minerals.	189
Silica in Sediments	23
Silica in Solution in the Presence of Soil and Related Material: Forms, Concentrations, and Reactions	195
Silica in Subsurface Waters of Some Parts of the Russian Platform.	21
Silica in Water. 1. Relation Between Ionic and Colloidal Silica.	131
Silica Precipitation From Alkaline Silicate Solutions	95
Silica Regimen and Diatomaceous Vegetation in the Lunz Lake and Neighboring Streams	162
Silica, Silixite, Silicification, and Growth of Crystals. . . .	145
Silica Solubility, 0°-200° C, and the Diagenesis of Siliceous Sediments	202

TitleItem No.

S

Silicate Incrustations Containing Serpentine.	78
Silicates: Reactivity With Sea Water	188
Silicic Acid and Silicates.	14
Silicic Acid Solutions. 2. $\text{SiO}_2\text{-NaOH-MgCl}_2$ Aqueous Solutions. .	72
Silicification of Rocks by Surface Waters	74
Silicon Content of the Gdansk Bay Waters.	199
Simple Aids in the Hydrothermal Investigation of Mineral Systems.	55
Sodium Silicates in Water to Prevent Corrosion.	215
Solubility and Forms of Occurrence of Silicic Acid in Solutions During Weathering Processes	183
Solubility and Transfer of Silica and Other Non-Volatiles in Steam	39
Solubility Equilibriums and the Rate of Solution of Quartz in Water at High Temperatures and Pressures.	178
"Solubility" of Albite in Hydrothermal Solutions.	111
Solubility of Amorphous Silica at 25° C.	148
Solubility of Amorphous Silica in Water	106
Solubility of Impurities Present in Water and Steam and Their Behavior in the Steam Tract of Power Stations	103
Solubility of Quartz and Sodium Metasilicate in Super-Heated Steam	135
Solubility of Quartz in Aqueous NaCl Solutions at High Temperatures and Pressures.	179
Solubility of Quartz in H_2O in the Range 1000-4000 Bars and 400-550° C.	163
Solubility of Quartz in Supercritical Water	107
Solubility of Quartz in Water at High Temperatures and Pressures.	141
Solubility of Quartz in Water in the Temperature Interval from 25° to 300° C.	149
"Solubility" of Silica.	129
Solubility of Silica.	130
Solubility of Silica.	143
Solubility of Silica and Alumina.	132
Solubility of Silica in Solutions of Electrolytes	173
Solubility of Silica in Water	108
Solubility of Silica in Water and Water Vapor	127
Solubility of Silicic Acid in Water and Steam and Its Effect on Silica Deposits in Turbines	87
Solubility of Solids in Gases	197
Solubility of Some Minerals in Superheated Steam at High Pressures	150
Solubility of the Chief Minerals of the Krivoi Rog Rock Series. .	198

Title

Item No.

S

Soluble Silica in Soils. 2. The Release of Monosilicic Acid from Soils	109
Solution Technique for Analysis of Silicates.	12
Solution, Transportation, and Precipitation of Iron and Silica.	93
Solutions of Silicates of the Alkalies.	133
Stability of Colloidal Gold Under Hydrothermal Conditions	113
Stability Relations of Some Minerals in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$	57
State of Silicic Acid in Aqueous Solutions.	206
States of Silica in Aqueous Solution. 2.	116
Storage of Sea-Water Samples for the Determination of Silicate.	9
Studies of the System Iron Oxide-Silica-Water at Low Oxygen Partial Pressures	37
Study of Colloidal Silica	169
Syntheses and Reactions of Mordenite.	33
Synthesis and Stability of Minerals in the System $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$	54
Synthesis of Clay Minerals.	43
Synthesis of Kaolin Clays at Normal Temperature and Pressure Conditions.	38
System $\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$	56
System Calcium Oxide-Silica-Water at 30°	154
System $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ and the Hydration of Calcium Silicates.	158
System $\text{KAlSiO}_4-\text{Mg}_2\text{SiO}_4-\text{SiO}_2-\text{H}_2\text{O}$ from 500 to 3000 bars and 800 to 1200° and Its Petrologic Significance.	46

T

Theoretical Aspects of the Dissolving Process of SiO_2 Preparations and of SiO_2 Minerals.	159
Thermodynamic Behavior of Quartz and Other Forms of Silica in Pure Water at Elevated Temperatures and Pressures With Conclusions on Their Mechanism of Solution	152
Thermodynamic Functions for the Solution of Silica in Water	117

U

Ultrabasic Liquids.	35
Upper Three-Phase Region in the System $\text{SiO}_2-\text{H}_2\text{O}$	139
Use of X-Ray Phase Analysis to Study Boiler Deposits.	73

W

Water-Soluble Silica.	156
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