LIV. THE BIOCHEMISTRY OF SILICIC ACID

V. THE SOLUTION OF SILICA AND SILICATE DUSTS IN BODY FLUIDS

By EARL JUDSON KING and MURRAY McGEORGE
From the British Postgraduate Medical School, London

(*Received 24 December 1937*)

THE presence of silica in blood, and the much larger amounts sometimes found in urine, indicate that silica is appreciably soluble in body fluids. The determination of such solubility, however, is a matter of considerable difficulty and different results have been obtained by various workers, owing to the operation of such variable factors as particle size, concentration of suspension, method of separation of solid from liquid phase and method of estimation of silica in solution. In addition, soluble silica is present partly in true molecular form and partly as a colloidal dispersion; and higher figures for solubility will be obtained if colloidal silica be included in addition to that present in true molecular solution.

It has been shown by Lucas & Dolan [1936: see also Briscoe *et al.* 1937] that under standard conditions up to periods of at least 2 weeks, both concentration of suspension and particle size have an important influence on the rate of solution of quartz.

The amount of silicic acid which a mineral form of silica such as quartz will yield in solution is exceedingly small when the mineral is present as crystals of ordinary dimensions, or as coarse fragments. But if it be reduced to a particle size of the order of the dust in the air, i.e. $<1\text{–}10\mu$, then the rate at which silica appears in solution becomes appreciable. While the evidence does not warrant the statement that the smaller the size of the particles the more quickly they dissolve, it is true that with "sized" particles more silica is yielded in solution in a given time by small particles than is obtained with the same weight of particles of a larger size. The amount dissolved also varies with the total amount of dust suspended in the liquid: at sufficiently low concentrations of dust the silica in solution is roughly proportional to the total amount of the solid phase. This simple proportionality is not maintained at higher concentrations of the solid, where a condition of apparent saturation may be approached.[1] The very low solubility figures recently recorded by Titus [1937] for quartz and sericite were obtained with small amounts of solid (10 mg. of dust per 100 ml.) and would undoubtedly have been greater had larger amounts of dusts been used. The total surface of solid exposed to the solvent probably determines the rate, if not the final amount of solution. The phenomenon of the solution of mineral particles might, in fact, be better considered as a leaching of material from the surfaces of the particles. In some cases (e.g. certain of the silicates)

---

[1] It is doubtful if the term "saturated solution" should be applied to systems of powdered silicate minerals suspended in water, since the total amount of silica dissolved varies not only with time and with the state of division of the solid phase, but may never attain that of a solution saturated with respect to freshly prepared silicic acid, even when a large amount of the most finely divided solid is shaken continuously with the solvent.

the leaching may be a preferential one, and the composition of the total solids passed into solution may not be identical with that of the mineral particles from which they came. This is the case not only in mineral dusts of mixed composition, but also (as found by Lucas & Dolan [1936] and Brammall & Leech [1937]) for some reputably pure mineral specimens: and mineralogists have repeatedly observed an interchange of ions between a solution and a solid mineral.

The method employed for the separation of the solid from the liquid phase is of fundamental importance in the determination of solubility of substances which are in a fine state of division. Simple filtration followed by gravimetric analysis is inadequate, since the small particles (present in mine and other dusts for instance) pass readily through the pores of the finest filter papers available, and figures for solubility thus obtained often include fragments of suspended material in addition to that in colloidal and molecular solution. The figures for silica appearing in the older literature are probably too high for this reason, as has been pointed out by Titus [1937].

Centrifuging at the moderate speeds (2000–4000 r.p.m.) attained with the ordinary type of centrifuge likewise fails to rid a solution completely of suspended particles. The results of Emmons & Wilcox [1937] have been criticized [King, 1937] on this basis, as giving an erroneous picture of the relative solubilities of silica dusts. With the size range of particles of 1–10μ, centrifuging at this sort of speed removes the larger particles but leaves in suspension the smaller ones, which will contribute their quota to the result of a gravimetric analysis of the supernatant fluid, and hence to the apparent solubility of the mineral dust investigated in this way. The polarizing microscope reveals large numbers of doubly refractile particles of 1–3μ in size after centrifuging at 3500 r.p.m. for 15 min. suspensions of quartz, flint, mine dust, mica and sericite in filtered blood serum, and analysis of the supernatants reveals the presence of large amounts of silica which are obviously not in solution. High-speed centrifuging (10,000–20,000 r.p.m.) completely removes these particles from suspension, and silica contents of the supernatant fluids are obtained, which are almost identical with that of the original blood serum before the addition of the dust.

A complete separation of the liquid from the solid phase can also be obtained by forcing the liquid through cellophane membrane [cf. Titus, 1937], but by this means not only all the suspended dust particles but also some of the colloidally dispersed silicic acid is taken out. The "free" (i.e. molybdic acid-reactible) and "total" silica of a high-speed centrifuging of a silicic acid solution are equal, but are considerably greater than that of an ultrafiltrate of the same solution. The difference probably represents silicic acid in a colloidal condition. It may be questioned whether this colloidal silicic acid should be included in a solubility figure. It reacts readily, however, with certain chemicals, e.g. molybdic acid, as if it were in true solution, and from the biologist's standpoint it is probably significant, since it is biologically available, e.g. in natural waters for the nutrition of phytoplankton.

While a gravimetric analysis of an improperly separated liquid phase will give a misleading figure, it is possible to gain a true measure of dissolved material by applying a method which involves a chemical reaction in which suspended particulate matter will not take part. Such a reaction is utilized in the silicomolybdic acid procedure for the colorimetric determination of silica. But in order to avoid any possibility of a solvent action by the reagents on suspended particles, it is preferable that they be completely removed before the reaction is applied. Both high-speed centrifuging and ultrafiltration have been used in the present work.

In the experiments to be described, "unsized" dust samples of mineral silicates have been used. It was desired not to attempt to obtain an absolute "solubility" figure, since it is contended that this term has not its usual significance when applied to these systems, but rather a measure of the amount of silica which would pass into solution in a body fluid from an excess of the powdered mineral containing the same proportion of finest particles, including ultramicroscopic, produced in the preparation of the dust. While it was not possible to procure exactly the same size distribution in the several mineral dusts used, there was in all a large proportion of particles in the smallest measurable category and under. It seemed desirable also to avoid the possibility of altering the samples in any way by exposure to a fluid, as in the washing process which would be necessary if they were to be separated by sedimentation into different size categories. It is felt that the results obtained give a valid comparison of the relative rates at which the different minerals will yield silicic acid in solution, when they are in a state of division similar to that obtaining in their air-borne dusts.

EXPERIMENTAL

Preparation of dusts.[1] The materials used are listed in Table I together with their origin and nature, and their size distribution in the powdered condition.

Table I. *Percentage size distribution of dust particles* (*in* μ)

Type and origin of dust	<1–3	3–6	6–10	10–15
Mineral specimens:				
Quartz, "Porcupine" (98·8 % SiO_2)	67	26	6	1
Quartz, pure (rock crystal—99·8 % SiO_2)	90	8	2	—
Flint (air elutriated sample—89 % SiO_2)	92	7	1	—
Felspar (air elutriated sample)	80	12	4	4
Asbestos		Teased fibres		
Sericite, "Georgia"	68	26	5	1
Sericite, "Ohio"	85	13	2	—
Sericitic schist, "Porcupine", 25 % fibrous sericite	88	10	2	—
Scotch Whinstone—basic rock (64 % SiO_2) containing labradorite, augite and serpentine, no free silica	76	16	4	4
Commercial preparations:				
Amorphous silica, precipitated (80 % SiO_2)		Large amorphous masses		
Fuller's earth	76	11	5	8
Kaolin	66	21	8	5
Talc	56	30	11	3
Air-borne dusts:				
Mine dust (South Africa)	75	15	7	3
Pennant Rock (produced by drilling) coal measure sandstone, 42 % free silica	85	14	1	—
Somerset Greys (produced by drilling) coal measure sandstone, 49 % free silica	82	15	3	—
Stone dust (used for stone-dusting underground)	80	18	2	—

Most of the minerals were hand-picked specimens of rock which were powdered in a mill, or in an agate mortar if the sample was small. Others were commercially prepared specimens of mineral material used industrially, and some were collected samples of air-borne dusts obtained from industry.

---

[1] For the samples of pure quartz and of fuller's earth we are indebted to Dr E. L. Middleton, for the quartz "porcupine" to Sir Frederick Banting, and for the air-borne dusts to Dr A. G. R. Whitehouse. The sericite "Georgia" and sericite "Ohio" were kindly sent us by Dr Leroy U. Gardner, and the sericitic schist by Dr G. Langford. The other specimens were from the collection of the late Prof. E. H. Kettle.

Particle size. Samples of dusts were "sized" by suspending a small quantity of each in water, evaporating to dryness on an electric hotplate a drop of each suspension on a glass slide, and measuring particle size by means of a graduated eyepiece at a magnification of 2500 diameters.

Glassware. In order to eliminate the possibility of silica being introduced into the solutions from the glass vessels, a coating of bakelite was applied to the interior surfaces. This is best accomplished by means of bakelite air-drying varnish (kindly supplied by Bakelite Ltd.). The flasks are cleaned with chromic-sulphuric acid mixture, well rinsed, and oven-dried. A flask is removed from the oven while still hot and is partly filled with the varnish, which is then slowly poured out while the flask is rotated. In this way a thin coating of the bakelite is evenly distributed over the interior. The flasks are left in an inverted position in a warm place for several days for the varnish to dry. A tough, firmly adherent layer of bakelite is formed which is acid- and alkali-resistant and which shows no tendency to peel or flake off even after prolonged exposure to liquids.

Solution of dusts in body fluids

Ascitic fluid was obtained from a case of congestive heart failure. Its composition in respect of electrolytes and other diffusible constituents was almost identical with that of blood plasma. The total protein was 0·22 %, and the *p*H 7·5. Blood was obtained from a case of hypertension with cerebral thrombosis. It was allowed to clot at 37° and the serum separated by centrifuging and decantation.

Both serum and ascitic fluid were preserved with 1 % of formalin. Previous trials had demonstrated that this did not alter in any measurable fashion the behaviour of these fluids towards silica dusts.

The samples of powdered minerals and dusts were weighed into the bakelited flasks and 100 ml. of fluid added. The flasks were closed with rubber bungs and were shaken mechanically in a water-bath at 37°. The *p*H of the mixtures was determined colorimetrically on the day of mounting and at intervals thereafter. In one case only, that of synthetic magnesium trisilicate, was there an alteration. All other mixtures remained at the original *p*H of the fluids. Samples of the mixtures were withdrawn at intervals for the determination of dissolved silica.

Separation of solid from liquid phase. Centrifuging was carried out in the special high-speed attachment of the International centrifuge. 5 ml. samples of the mixtures from the flasks were placed in the special 7 ml. glass centrifuge tubes, and were spun at 15,000–20,000 r.p.m. for 30 min. This treatment completely removed suspended material. 3 ml. samples of the supernatant liquids were carefully withdrawn for analysis.

Ultrafiltration of the mixtures was accomplished by submitting 6 ml. samples to a pressure of 10 atmospheres in a special Seitz filter fitted with a cellophane membrane mounted between filter papers. The cellophane membranes were prepared by soaking them for 48 hr. in alcohol and afterwards in water, to remove some impurity, the presence of which gave rise to an appreciable blank in the colorimetric silica method. While the porosity size of these membranes was not known for certain, it must have been very small, since all the protein—albumin as well as globulin, was removed from both ascitic fluid and blood serum.

Determination of silica. (Method of King & Stantial [1933].) 3 ml. portions of the supernatant liquids from the centrifuging or of the ultrafiltrates were treated in 100 ml. conical flasks with 6 ml. of the ferric chloride[1] and 6 ml. of the sodium acetate[2] solutions. The mixtures were brought quickly to the boil, with vigorous shaking, and were filtered hot. 10 ml. of the cooled filtrates were placed in 15 ml. volumetric flasks, 1·2 ml. of molybdate[3] and 0·3 ml. of aminonaphtholsulphonic acid[4] solution added, and water to 15 ml. Standards[5] of 0·01, 0·02 and 0·05 mg. SiO_2 were prepared at the same time. The coloured solutions were mixed and allowed to stand for 5 min. The colours were compared in a Duboscq type colorimeter fitted with an Osram sodium light. Comparison in monochromatic yellow light greatly increased the accuracy as well as the ease of the colorimetric determination. The results were calculated to show the amount of dissolved silica in mg. contained in 100 ml. of fluid.

RESULTS

Solution of quartz in blood serum and ascitic fluid

Human blood serum, in amount sufficient for these experiments, was impossible to obtain. Serum, moreover, has several disadvantages for use in an experiment which requires regular sampling. It is difficult to keep sterile without an aseptic technique; its high protein content causes difficulties in the analytical manipulations; and it tends to become more viscous on prolonged standing at 37°. Ascitic fluid (or "dropsy fluid") is easily obtainable in large volumes from hospital cases, and its use presents fewer technical difficulties in the analytical procedures. In order to determine if ascitic fluid gave results comparable with blood serum an experiment was made in which the solution of pulverized rock crystal was followed in the two liquids for 18 days. Separation of solid from liquid was made in samples by high-speed centrifuging. Table II shows that silica appeared more quickly in solution in the ascitic fluid but that the final results were substantially the same.

Table II. *Solution of powdered rock crystal in blood serum and ascitic fluid (mg. SiO_2 per 100 ml.)*

Days ...	1	2	3	5	7	12	18
Ascitic fluid	6·1	8·0	8·4	9·0	9·1	9·1	9·1
Blood serum	2·1	3·4	4·5	5·8	8·2	8·7	8·9

Effect of the concentration of solid on the amount of silica dissolved

Varying the amounts of the solid phase from 25 mg. of rock crystal dust in 100 ml. of ascitic fluid to 2 g. per 100 ml. led to a progressive increase in the amount of silica in solution in the lower concentrations. Above 0·5 g. per 100 ml. the final figures for soluble silica were about the same, but the curve of solution

---

[1] 1% $FeCl_3$, $6H_2O$ in 0·02 *N* HCl.

[2] 1·5% $C_2H_3O_2Na$, $3H_2O$ in 0·028 *N* NaOH. (The NaOH, to be silica-free, must be prepared from metallic sodium: B.D.H. "sodium hydroxide pure (from sodium)" is satisfactory.)

[3] 5% ammonium molybdate in *N* H_2SO_4.

[4] 0·2% 1:2:4-aminonaphtholsulphonic acid in 2·4% Na_2SO_3, $7H_2O$ and 12% $NaHSO_3$.

[5] 31·4 mg. Na_2SiF_6 dissolved in 1 l. of water give a standard solution containing 0·01 mg. SiO_2 in 1 ml. A fresh standard should be made once a week.

The original article should be consulted for details of the preparation of solutions, and for the precautions which must be observed in the use of the method.

was steeper and the apparent "saturation" approached more quickly the larger the amount of solid used. The results obtained are graphically presented in Fig. 1.

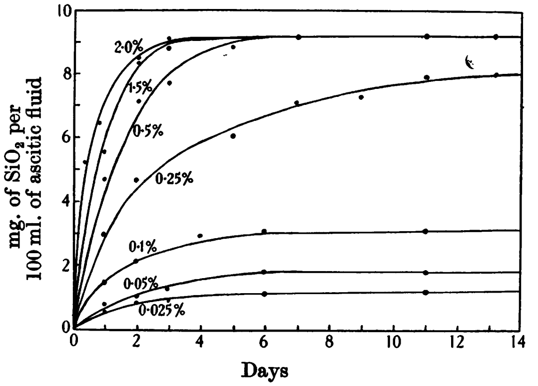

Fig. 1. Effect of concentration of solid on the solution of silica. Percentage figures represent g. of rock crystal dust suspended in 100 ml. of ascitic fluid.

The solution of freshly prepared silicic acid

It was of interest to determine how the amount of silicic acid dissolved from a mineral form of silica would compare with that from the most readily soluble form of free silica, namely freshly precipitated silicic acid. The calculated amounts of sodium silicate (Na_2SiO_3, $5H_2O$) to give 2 and 5 g. of SiO_2 as silicic acid were dissolved in water in 250 ml. centrifuge bottles, and a slight excess over the calculated amount of conc. HCl was added. The mixtures were shaken and left for several hours. The flocculated precipitates of gelatinous silicic acid were spun down and washed well with distilled water. They were finally centrifuged at 4000 r.p.m. for 30 min., and the well-packed precipitates stirred up and shaken with 100 ml. of ascitic fluid. The mixtures were shaken at 37° and samples taken for analysis at intervals over the next 72 hr. Very little difference between the rates of solution of the two samples was found.

The production of silicic acid in solution was very rapid, and the maximum solubility figure was rapidly attained. The results are set out in Table III. It is of note that the final figure of 9 mg. SiO_2 per 100 ml. is the same as that obtained for a similar suspension of precipitated silicic acid in a different ascitic fluid which had been kept for 6 months with occasional shaking. The maximum solubility figure obtained with the finely powdered rock crystal is also practically identical: this is of particular interest in that it shows that at least one mineral form of silica, provided that it be in a sufficiently fine state of division, is capable of yielding as much silicic acid in solution as can be obtained from a chemically prepared specimen of the readily soluble amorphous variety.

Table III. *Dissolution of freshly precipitated silicic acid*

(mg. SiO_2 per 100 ml. ascitic fluid)

Hr. ...	2	5	18	24	48	72
SiO_2 dissolved	5·8	6·9	8·0	8·8	9·0	9·1

Comparison of solubility determinations following high-speed centrifuging and ultrafiltration

All estimations of soluble silica were made on both centrifuged and ultrafiltered samples. In the majority of cases only the results for the centrifuged samples are given. In every instance where an appreciable solubility figure was obtained the centrifugate gave a higher result than the ultrafiltrate. The difference was in general greater the larger the figure for dissolved silica. Amorphous silica preparations always showed a greater difference than the crystalline mineral varieties. The ultrafiltrate figures for the solution of precipitated silicic acid were occasionally as much as 30 % lower than the figures for the centrifugate. The results for some of the determinations on representative dusts are set out in Table IV. The filtrate figures for amorphous silica and for quartz show day-to-day fluctuations which are in contrast to the regularity of the figures obtained for the centrifugates. This phenomenon was repeatedly observed. It is believed to be due to a reversible transition of the dissolved silicic acid from the molecularly dispersed state to the colloidal. Both forms are determined by the silicomolybdic acid method, and both are present in the centrifugate. But at least part of the silicic acid in colloidal solution appears to be removed by filtration through the cellophane membranes used.

Table IV. *Comparison of solubility determinations following high-speed centrifuging and ultrafiltration*

	Amorphous silica dry		Pure quartz		Flint		Fuller's earth	
Days	C.	F.	C.	F.	C.	F.	C.	F.
1	5·2	3·6	3·8	2·8	—	—	1·4	1·0
2	5·6	4·3	7·7	5·6	5·0	4·1	1·4	1·1
3	5·7	4·3	7·8	6·8	6·1	4·8	1·4	1·1
5	6·4	4·6	7·8	7·0	6·2	5·0	1·3	1·0
8	6·4	4·3	7·8	6·9	6·4	5·1	1·3	1·0
10	6·8	4·9	—	—	—	—	1·2	1·1
13	6·5	4·7	7·8	6·6	—	—	1·2	1·0
21	6·8	4·8	—	—	—	—	—	—

"C.": Removal of solid phase by high-speed centrifuging at 20,000 r.p.m. for 30 min.

"F.": Removal of solid phase by ultrafiltration through cellophane membrane under pressure of 10 atmospheres.

Figures represent mg. SiO_2 in 100 ml. of ascitic fluid.

The silica of natural waters also seems to be partly in colloidal solution. Several samples of fresh and salt water were centrifuged and ultrafiltered. In those which had a sufficient concentration of silicic acid to be determinable by the method employed, the same phenomenon was observed, i.e. part of the analysable silicic acid was removed by the membrane.

Solution of silica and silicate dusts in ascitic fluid

Samples of the dusts described in Table I were tested for their solution rates over a period of a month. Samples were withdrawn daily for the first week and thereafter at increasing intervals. The results for representative days are given in Table V and Fig. 2.

Table V. *Solution of silica and silicate dusts in ascitic fluid*

Type of dust	Solubility—mg. per 100 ml.					
	1 day	2 days	5 days	8 days	Maximum solubility	
	Separation by high-speed centrifuging					By ultra-filtration
Mineral specimens:						
Quartz, "Porcupine"	1·3	2·0	4·0	4·6	6·4	4·8
Quartz, pure rock crystal	7·6	8·0	9·0	9·1	9·1	7·0
Flint	5·0	6·1	6·2	6·4	6·5	5·6
Felspar	0·5	0·5	0·6	0·7	0·8	0·6
Asbestos	—	1·1	1·3	1·5	1·6	1·2
Sericite—"Georgia"	0·3	0·3	0·4	0·4	0·4	0·4
"Ohio"	0·5	0·5	0·5	0·5	0·6	0·5
Sericitic schist	0·5	0·6	0·7	0·8	0·8	0·7
Scotch Whinstone	0·8	0·9	1·0	1·0	1·0	0·8
Commercial preparations:						
Amorphous silica—desiccated	5·2	5·6	6·4	6·8	7·0	4·8
freshly prepared	8·0	8·6	8·8	8·9	9·0	6·3
Magnesium trisilicate	3·5	3·6	4·0	4·2	4·4	3·2
Fuller's earth	1·2	1·2	1·3	1·3	1·4	1·0
Kaolin	0·3	0·3	0·4	0·4	0·4	0·3
Talc	0·5	0·6	0·8	0·8	0·8	0·7
Air-borne dusts:						
Mine dust (South Africa)	0·5	0·6	0·8	1·0	1·1	1·0
Pennant Rock (from drilling)	0·6	0·6	0·7	0·8	0·8	0·7
Somerset Greys (from drilling)	0·6	0·6	0·7	0·7	0·7	0·7
Stone dust (for dusting)	0·5	0·6	0·6	0·6	0·6	0·6

2% suspensions maintained at 37° with constant agitation.

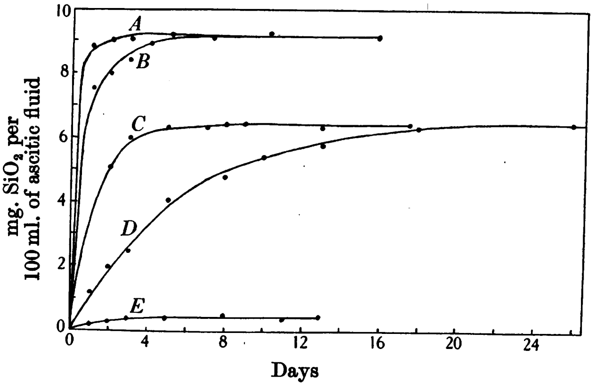

Fig. 2. Solution of silica and silicate dusts in ascitic fluid: 2 g. of dust in 100 ml. of fluid at 37°. *A*, freshly prepared amorphous silica; *B*, pure quartz (rock crystal—very finely ground); *C*, flint; *D*, quartz (Porcupine); *E*, sericite.

The effect of depressors of solubility

It was shown by Denny *et al.* [1937] that several substances, notably aluminium, would greatly depress the amount of silicic acid yielded in solution by various forms of silica. Briscoe *et al.* [1937] noted a similar effect for calcium oxide. The effect on dissolved silica of certain metallic oxides and hydroxides ($Ca(OH)_2$, MgO, Fe_2O_3, $Al(OH)_3$, SrO, $Be(OH)_2$) had been noted by the author in the study of precipitants for phosphate in the colorimetric molybdic acid method of estimation. These oxides had all proved unsuitable for phosphate elimination because of the fact that they precipitate and lead to the loss of variable amounts of silicate ion. The solubility depressor effect is believed by the authors to be simple precipitation of the insoluble silicate of the metal in the presence of an excess of the hydroxide. This effect is only obtained in alkaline solutions. Whether the effect of metals, e.g. aluminium, is to be explained in the same way or on the basis of some more complex explanation, is not clear. Some results illustrating the depression of solution of silica are shown in Table VI.

Table VI. *Depression of solution of quartz by aluminium and iron*

(mg. SiO_2 dissolved by 100 ml. ascitic fluid)

Days ...	1	2	3	4	5	6	7	8
Quartz	3·8	7·7	7·8	8·0	—	7·8	7·8	8·0
Quartz + 1 % aluminium	0·5	0·6	0·6	0·5	—	0·5	—	—
Quartz + 2 % alumina	0·6	0·5	0·6	0·6	—	0·7	0·6	0·7
Quartz + 1 % reduced iron	1·0	1·2	1·6	2·2	—	2·9	3·0	3·5

Discussion

The chief point of interest emerging from an inspection of these figures is the relatively greater rate of solution of the free forms of silica, as compared with the silicates. With only one exception, that of the synthetic magnesium trisilicate, the silicates yielded very small amounts of dissolved silicic acid. Whether or not this is a general phenomenon cannot be stated from the study of a small number of minerals. But it seems a reasonable assumption that the solution of an alkali or an alkaline earth silicate would be slow in an alkaline medium; whereas the acid nature, feeble though it may be, of the free oxide of silicon might be expected to favour its solution in fluids of a mildly alkaline reaction.

Summary

A study has been made of the solution of silica and silicate dusts in body fluids. The amount of silicic acid yielded in solution is determined, among other things, by the amount of solid used. Blood serum and ascitic fluid dissolve about the same amount of silica, but the rate of solution is slower in the former. Some mineral forms of silica (quartz) yield as much silica in solution as is obtained with freshly precipitated gelatinous silicic acid. Part of the dissolved silica, probably that in colloidal solution, is removed by ultrafiltration. The free forms of silica appear to dissolve more readily than the silicates studied.

The authors are indebted to the Medical Research Council for a grant to defray the costs of this investigation.

REFERENCES

Brammall & Leech (1937). *Bull. Instn Min. Metall., Lond.*, April and June.
Briscoe, Matthews, Holt & Sanderson (1937). *Bull. Instn Min. Metall., Lond.*, April and June.
Denny, Robson & Irwin (1937). *Canad. Med. Ass. J.* **37**, 1.
Emmons & Wilcox (1937). *Amer. J. Min.* **22**, 256.
King (1937). *Nature, Lond.*, **140**, 320.
—— & Stantial (1933). *Biochem. J.* **27**, 990.
Lucas & Dolan (1936). *Canad. Chem. Metall.* **20**, 185.
—— —— (1938). (In press.)
Titus (1937). *J. industr. Hyg.* **19**, 138.