CCXCI. THE BIOCHEMISTRY OF SILICIC ACID

VII. DEPRESSION OF THE APPARENT SOLUBILITY OF SILICA IN BODY FLUIDS

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THE depression of solubility of SiO_2 through the agency of various metals and metallic oxides, notably Fe and Al, was briefly referred to in a former communication [King & McGeorge, 1938]. It was suggested that the apparent decrease in solubility of quartz and amorphous SiO_2 was due to precipitation of the dissolved silicic acid as the insoluble silicate of the metal. The phenomenon has now been explored further, and the effects of various mineral dusts on the solution of SiO_2 from quartz have been investigated.

Most of the mineral silicates are much less soluble in blood serum and ascitic fluid than are the free forms of SiO_2 . Kaolin is particularly insoluble. In a mixture of kaolin and quartz powder suspended in a liquid it might be expected that the amount of SiO_2 dissolved would be conditioned by the most active member of the mixture, and that in the presence of an excess of the mixed powder the solubility would approach that of quartz powder taken alone. Naturally occurring kaolins, such as those represented in shales, contain variable, sometimes large, amounts of free SiO_2 , and yet these natural stone dusts have an exceedingly low solubility. The amount of free SiO_2 represented in a sample of stone dust would lead to much more solution of silica if suspended alone in the same volume of liquid. This fact was brought out in the previous communication where it was shown that a stone dust (shale—used for mine dusting) had a solubility of less than 1 mg./100 ml. although it contained about 40 % free SiO_2 , whereas the 0.8 g. free SiO_2 present in the 2 g. stone dust taken for 100 ml. ascitic fluid would if taken separately dissolve to the extent of 9 mg./100 ml. The figures set out in Table I demonstrate these points more fully. The methods used in this investigation—preparation and examination of dusts, solution experiments, separation of solid from liquid phase, determination of dissolved SiO_2 etc.—were those described in the previous communication [King & McGeorge, 1938]. The silicate minerals are much less soluble than quartz in the ascitic fluid used,¹ and the stone dusts are only slightly soluble despite their free SiO_2 contents which in some cases are large. The SiO_2 dissolved from the coal and coal-mine dusts is, of course, related to the silicate minerals contained in them, and is of the same order as that from the stone dusts.

The apparent depression of the solution of free SiO_2 contained in the stone dusts suggested that the effect might be extended to quartz admixed with the stone dust. This proved to be the case as is shown in Table II. The addition of increasing amounts of stone dust to 2 g. quartz suspended in 100 ml. ascitic fluid led to a progressive decrease in the SiO_2 dissolved, from 7 mg. SiO_2 /100 ml. to

¹ This ascitic fluid was of a more alkaline reaction (pH 8.0) than that used in the previous investigation, and the figures for solubility of the various dusts are hence not identical with those recorded in the previous paper.

Table I. *Dissolution of silica from mineral dusts*

2 g. dust suspended in 100 ml. ascitic fluid at 37°

Mg. SiO₂ per 100 ml.

Mineral dusts:	1 day	3 days	6 days
Quartz	4.4	5.4	7.0
Sericite	—	1.7	1.6
Chlorite (Mass.)	—	1.1	1.4
Chlorite (Saxony)	—	1.0	1.2
Kaolin	0.1	0.1	0.1
Biotite	—	1.0	1.1
Stone dusts:			
D. and C., S. 194* (39 % free SiO ₂ , 10.8 % Al)	0.5	0.6	0.6
C. and W., S. 20* (7 % free SiO ₂ , 13.5 % Al)	0.6	0.9	1.5
P. and P., S. 31* (21 % free SiO ₂ , 9.1 % Al)	1.4	1.5	1.3
Somerset Greys† (49 % free SiO ₂ , 7.2 % Al)	2.2	2.1	2.0
Pennant Rock† (42 % free SiO ₂ , 5.9 % Al)	2.4	2.5	2.2
Air-borne coal-mine dusts:			
Am. D. (16 % ash)	1.2	1.4	1.4
Am. E. (39 % ash)	1.5	1.4	1.1
Am. I. (18 % ash)	1.2	1.4	1.8
Am. J. (25 % ash)	0.8	1.3	1.4
Coal dusts:			
Am. anthracite (3.9 % ash)	0.9	1.5	2.0
Cy. bottom coal (2.5 % ash)	1.5	2.1	2.1
Ba. soft coal (4.5 % ash)	1.7	1.6	1.8
Yn. anthracite (6.3 % ash)	1.5	1.2	1.4

* Shale dusts used for dusting underground.

† Coal-measure sandstones, produced by drilling.

Table II. *Dissolution of silica from mixtures of quartz and mineral dusts*mg. SiO₂ dissolved by 100 ml. ascitic fluid

	1 day	3 days	6 days
2 %* Quartz (alone)	4.4	5.4	7.0
2 % D. and C. stone dust (alone)	0.5	0.6	0.6
2 % Quartz + 1 % stone dust	3.2	3.4	4.6
2 % Quartz + 2 % stone dust	1.8	1.7	2.4
2 % Quartz + 4 % stone dust	1.6	1.4	1.7
2 % Yn. coal dust (alone)	1.5	1.2	1.4
2 % Quartz + 2 % coal dust	2.9	2.6	3.7
2 % Quartz + 4 % coal dust	2.2	1.8	2.2
2 % Kaolin (alone)	0.1	0.1	0.1
2 % Quartz + 2 % kaolin	2.7	4.6	4.5
2 % Quartz + 4 % kaolin	1.8	2.3	2.4
2 % Quartz + 1 % Al ₂ O ₃	0.4	0.3	0.3

* The % figures (e.g. 2 % quartz) denote the number of g. dust per 100 ml. ascitic fluid.

1.7 mg. when twice as much stone dust as quartz was present. The phenomenon, moreover, seemed to be a general one, as a similar depression was obtained with several stone dusts and silicate minerals (Table III).

Coal dust, and the air-borne dusts from coal mines, appear to depress SiO₂ solubility in proportion to their silicate mineral content. Pure carbon (Kahlbaum's "carbo activ") and charcoal of low ash content have no effect on the solution of quartz. The depressions seen in Table IV would seem, therefore, to depend on the presence of stone dust in the coal. One of the coal dusts (Cy.) differs from the others in that it causes an increase in the amount of SiO₂ dissolved. This dust probably differs also from the others in the nature of its siliceous constituents.

Table III. *Effect of mineral dusts on the dissolution of quartz*% reduction in amount of SiO_2 dissolved from 2 g. quartz in 100 ml. of ascitic fluid

	1 day	3 days	6 days
Sericite (2 g.)	—	49	61
Biotite (2 g.)	—	79	81
Chlorite (Mass.) (2 g.)	—	80	78
Chlorite (Saxony) (2 g.)	—	81	81
Kaolin (1 g.)	3	0	18
Kaolin (4 g.)	59	62	64
Al_2O_3 (1 g.)	90	96	96
Al_2O_3 (4 g.)	96	98	97
D. and C. stone dust (1 g.)	28	38	27
D. and C. stone dust (2 g.)	58	69	66
C. and W. stone dust (1 g.)	28	20	32
C. and W. stone dust (2 g.)	39	38	40
P. and P. stone dust (1 g.)	44	37	50
P. and P. stone dust (2 g.)	55	61	64
Somerset Greys (1 g.)	23	36	37
Somerset Greys (2 g.)	28	44	57
Pennant Rock (1 g.)	37	44	56
Pennant Rock (2 g.)	42	44	65

Table IV. *Effect of coal dust on the dissolution of quartz*2 g. quartz, 4 g. coal dust per 100 ml. ascitic fluid; % reduction in amount of SiO_2 dissolved

	1 day %	3 days %	6 days %
Am. D. air-borne dust (16% ash)	23	6	21
Am. E. air-borne dust (39% ash)	53	63	75
Am. I. air-borne dust (18% ash)	33	50	54
Am. J. air-borne dust (25% ash)	71	64	71
Am. anthracite (3.9% ash)	40	30	35
Ba. soft coal (4.5% ash)	54	55	62
Yn. anthracite (6.3% ash)	51	69	69
Cy. bottom coal (2.5% ash)	(11)	(34)	(5% increase)

Depression of solubility of SiO_2 by these dusts may be dependent on adsorption of the dissolving silicic acid, on its precipitation as an insoluble silicate, or on the coating of the silica particles by some constituent of the depressor. In Table V are shown the results of adding silicate and mixed stone dusts to a saturated solution of SiO_2 in ascitic fluid which had been previously filtered free of all suspended particles. The depression of the amount of dissolved SiO_2 by the various mineral dusts is here clearly a case of precipitation or of adsorption. The SiO_2 dissolved in the liquid may react with some constituent of the mineral dust to form an insoluble precipitate. The coating of the solid particles of SiO_2 by a layer of the "depressor", e.g. of $\text{Al}(\text{OH})_3$, would account for the depression of solubility shown in Table III, but this sort of mechanism cannot furnish a satisfactory explanation of the precipitation of dissolved SiO_2 shown in Table V. Further work on the composition of the solid phase of these mixtures should reveal an enrichment of the dust in SiO_2 , and may possibly reveal the nature of the change taking place. Most mineral silicates are not of rigidly uniform composition, and it is possible that many of them may be capable of reacting with excess free SiO_2 with a consequent formation of a complex of higher SiO_2 content than the original.

The precipitation of SiO_2 from its solution by dusts from coal mines is shown in Table V. The results are somewhat irregular. No well-defined relationship is seen between the amount of depression of the SiO_2 in solution and the ash content. But the precipitation of dissolved SiO_2 has nevertheless almost certainly been

Table V. *Precipitation of dissolved silica by mineral dusts*

Decrease of dissolved SiO_2 in a "saturated solution" of quartz in ascitic fluid, 9 mg./100 ml., due to added dust

	g. dust added per 100 ml.	% decrease in dissolved SiO_2		
		1 day	3 days	6 days
Sericite	2	—	24	17
Biotite	2	—	33	35
Chlorite (Mass.)	2	—	76	75
Chlorite (Saxony)	2	—	69	66
Kaolin	2	32	29	26
	4	38	26	32
Al_2O_3	2	94	94	94
	4	95	95	96
D. and C. stone dust	2	24	31	38
	4	36	44	54
C. and W. stone dust	2	40	53	—
	4	46	50	—
P. and P. stone dust	2	27	25	18
	4	37	21	27
Somerset Greys	2	11	10	24
	4	22	20	30
Pennant Rock	2	8	5	12
	4	7	14	30
Am. D. air-borne dust	2	6	1	0
	4	9	4	4
Am. E. air-borne dust	2	4	21	20
	4	14	18	21
Am. I. air-borne dust	2	8	12	—
	4	16	23	12
Am. J. air-borne dust	2	20	—	7
	4	27	21	21

brought about by the minerals contaminating the coal. It is possible that adsorption of silicic acid by the carbonaceous particles of coal dust may play a part in the retardation of solution of SiO_2 and in the precipitation of SiO_2 already existing in solution, but this is unlikely since activated charcoal is without effect. The carbonaceous constituents of the coal may, however, affect the solubility of SiO_2 in an indirect manner, through an interaction (e.g. by adsorption) with some of the constituents of the ascitic fluid. Whether an adsorptive effect plays a part in the phenomenon of depression by coal dust of SiO_2 solubility, as well as the possibility of a reaction of the dissolved SiO_2 with different constituents of the dust will form the subject of further investigation.

The stone dusts used in this study¹ were samples of dust which have long been used for the stone-dusting of coal mines in Great Britain with the purpose of diminishing the hazard of explosion. Industrial experience during many years has led to the belief that stone-dusting in coal mines has not introduced or increased the silicosis hazard. Indeed the belief has slowly evolved that stone-

¹ The stone dusts were furnished by Dr A. G. R. Whitehouse, of the Safety in Mines Research Laboratory, who finds them to have a depressing action on the solution of free SiO_2 in Na_2CO_3 solution [1938], and with whom the authors have been fortunate to be in collaboration. The mineral dusts—sericite, chlorite, biotite and kaolin—were kindly given us by Dr A. Brammall, and the air-borne coal-mine dusts by Prof. H. V. A. Briscoe.

dusting actually diminishes the risk of silicosis in mines [cf. Haldane, 1917; 1931], and that certain mineral silicates may off-set the action of quartz in its relation to the disease. Recent experimental work on the effect of mineral dusts on the lungs and other tissues of animals [Gardner, 1938] has appeared to indicate that many mineral silicates may modify and even retard the action of free SiO_2 . The finding that certain stone dusts modify the silicosis hazard may have its explanation in the experimental findings reported here, but at the present time it can only be interpreted as an interesting parallel which merits further study.

SUMMARY

The presence of shale and of some other silicate minerals may markedly diminish the amount of SiO_2 dissolved from a mixed rock dust in ascitic fluid. The amount of SiO_2 dissolved from quartz is reduced, and SiO_2 is removed from solution in the presence of these silicates.

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