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Silica in hot-spring waters*

Donald E. White, W. W. Brannock, and K. J. Murata
U.S. Geological Survey, Washington 25, D.C.

Contents

Abstract—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 two or three 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 p.p.m. at 90°C and 110 p.p.m. 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

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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 ⇌ 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.

Introduction

History of the investigation. In 1947, K. J. Murata found that the quantity of silica determinable by standard colorimetric methods in aged-water samples from Steamboat Springs, Nevada, was much less than total silica determined gravimetrically. A few measurements by Murata and White at the springs with a visual comparator demonstrated the fact that colorimetrically determinable silica in fresh samples was approximately equal to the gravimetric determinations. Brannock and White then made a series of detailed measurements in 1948 on fresh and aged samples, using a portable battery-operated colorimeter.

In samples of high-silica waters that were aged at room temperature, some of the silica became nonreacting to the colorimetric reagent, molybdate, but the nature of the reacting silica remained uncertain until Weitz, Franck, and Schuchard (1950), and Alexander, Heston, and Iler (1954) demonstrated that monomeric silicic acid reacts completely with molybdate in about 75 sec. but that dimeric and polymeric silicic acids require 10 min or more.

In 1954 Konrad B. Krauskopf started laboratory experiments that were designed to clarify some of the relationships we had found in natural waters. His results, published in a separate paper (1956), agree strikingly with ours. His paper should be consulted for a review of previous work, for definition of terms, and for general principles applicable to our study, which is concerned largely with the behaviour of silica in nature.

Methods. The values for dissolved (monomeric) silica and most total silica reported by the authors were obtained colorimetrically by methods based on the formation of the yellow silicomolybdate complex. The measurements were first made by visual comparison with a series of empirical standards, and in later work with a portable photo-electric colorimeter that was taken into the field.

For those determinations of dissolved silica in which the photo-electric colorimeter was used, measurements were made on solutions which contained 10 ml of water sample and 10 ml of reagent solution diluted to a total volume of 110 ml with distilled water. The reagent solution

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was a 5% solution of ammonium molybdate in 2 N hydrochloric acid. The temperature of the distilled water was adjusted prior to mixing so that, upon mixing, the temperature of the resulting solution was approximately 32°C (90°F). Within three minutes after mixing, the yellow colour of the solution reached maximum intensity and remained constant for about 5 min. The reading at maximum intensity was referred to a standard curve, and after a blank correction was made for silica in the reagents and the distilled water, the concentration of dissolved silica in the sample was obtained.

The standard curve was based on readings obtained when a series of solutions containing known amounts of silica, prepared by fusion of quartz powder with sodium carbonate, were carried through the procedure described above for the determination of dissolved silica.

In the determination of total silica, 150 mg of sodium hydroxide was added to 10 ml of water sample, and the resulting solution was boiled for 5 min, neutralized with hydrochloric acid, and carried through the same procedure as that used in the determination of dissolved silica.

The determination of dissolved silica was generally reproducible within 5 p.p.m. Fifteen comparisons were made between dissolved silica in fresh samples and total silica in the same samples, determined colorimetrically within two days after collection. Only four of the fifteen differed by more than 5 p.p.m. and two by more than 7 p.p.m. Total silica was also determined in eight aged samples by gravimetric as well as by colorimetric methods. On the average, the gravimetric value was 13 p.p.m. greater than the colorimetric. As discussed later, the reason for the discrepancy is not known, but it may be a lessening of colour intensity with increasing salinity. A salt-factor correction of 1·23 times the apparent content is necessary for sea water (CHOW and ROBINSON, 1953).

RELATIONSHIPS AT HOT-SPRING VENTS

Dissolved silica. The content of dissolved silica (here used synonymously with monomeric silica or monosilicic acid, in contrast to polymeric or colloidal silica) in vent samples is identical to total silica determined colorimetrically, within the limits of accuracy of the methods (see Tables 1 and 2).

Colloidal silica. WHITE has observed colloidal silica in vent samples from two springs in Norris Basin of Yellowstone Park and also at Haukadalur and Hveravellir in Iceland. The waters are slightly opalescent in sunlight, but not turbid. They are all exceptionally high in total silica, ranging from 500 to 700 p.p.m. Upon standing, they become much more opalescent, in contrast to acid springs of somewhat similar appearance that become clearer with settling of suspended clay.

Measurements at Porcelain Terrace, Yellowstone National Park (see Table 2), prove that, even in the highest-silica waters, most of the silica of fresh samples is dissolved in the monomeric form, but a little is colloidal. In other springs, when colloidal particles form at high temperature, they generally grow rapidly to super-colloidal size and precipitate as gelatinous silica.

Gelatinous silica. Total silica as used in this paper includes silica in solution and in colloidal suspension. A few springs at Steamboat Springs contain gelatinous silica that is transported in mechanical suspension but that settles when rate of movement is sufficiently slow. This siliceous sediment is notable for its high content of antimony, mercury, gold, and silver (BRANNOCK *et al.*, 1948, p. 222–223) and is flushed out of the spring system in abundance at times of high discharge.

Of the Steamboat Springs shown in Table 1 and Fig. 1, springs 21, 24, and 50 were depositing much gelatinous silica in or immediately below the spring vents; lesser amounts were depositing from springs 2, 3, 4, 8, 16, 18, 19n, 23, and 44.

Solubility and temperature. In Fig. 1, the dissolved silica of vent samples has been plotted against temperature when collected. Although many points suggest a random scattering, only three are significantly above the solubility of amorphous silica as indicated by the compilation of ALEXANDER *et al.* (1954, p. 453), and most are somewhat lower. An approximate solubility curve for hot springs is indicated on Fig. 1. This curve was drawn through the equilibrium point for samples aged at
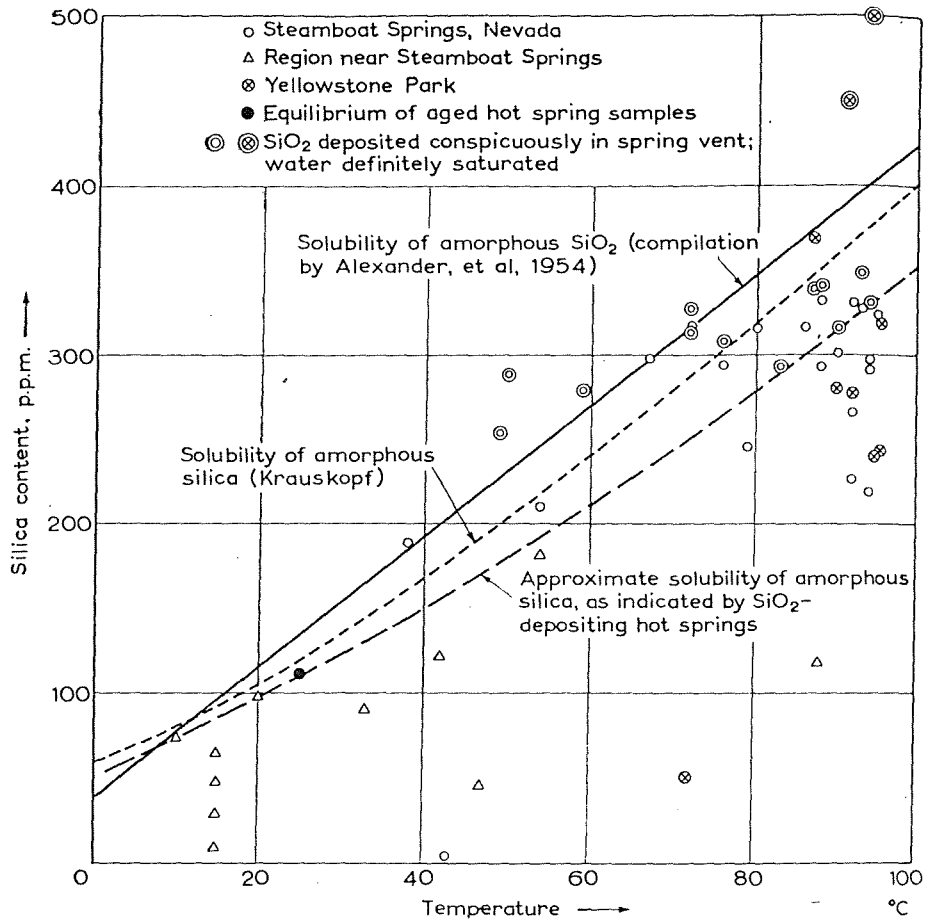
Fig. 1. Relation of dissolved silica and temperature of water at time of collection.

room temperature (discussed later in detail), and the points for springs 23, 18, and 21, which are depositing gelatinous silica. All springs known to discharge gelatinous silica at their vents are believed to be saturated or supersaturated with respect to amorphous silica. All waters above the approximate solubility curve were probably supersaturated, even though some were not depositing gelatinous silica; most of the waters below the line were probably unsaturated with respect to amorphous silica, although some may have been slightly supersaturated. It should be emphasized that a precise solubility curve cannot be determined by this method.

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The indicated solubility for amorphous silica in hot-spring water is slightly lower than the solubility found by KRAUSKOPF (1956). In the hot-spring samples, no correction has been made for the salt effect described by CHOW and ROBINSON

Table 1. Silica content of hot springs and miscellaneous waters, Steamboat Springs area, Nevada. Dissolved silica determined by the colorimetric method within five minutes after collection of the samples.

Spring	Date Collected	Temp. °C[1]	pH[2]	Cl, p.p.m.[3]	Total SiO_2, p.p.m.[4]	Dissolved SiO_2, p.p.m.	Comments
1	9/24/48	88	7·98	868		332	
1n	9/24/48	92	6·37	872		331	
2	9/24/48	87	6·28	912		339	Some gelatinous SiO_2 in spring
3	9/24/48	72	6·46	918		327	Some gelatinous SiO_2 in spring
4	9/24/48	49	5·82	996		254	Some gelatinous SiO_2 in spring Some drainage from 5
5	9/24/48	93	6·96	972		324	
5	10/2/48	95	7·34	926	330	324	
6	9/24/48	79	6·91	924		256	Discharge pt. for 7
7	9/24/48	92	6·59	906		266	
8	9/22/48	72	7·54	850		313	Some gelatinous SiO_2 in spring
9	9/22/48	67	6·10	844		298	
10	9/22/48	72	5·85	840		316	
14	9/14a/48	80 ±	5·10	566		258	
14	9/22/48	68	5·03	572		247	
14	10/2/48	92	5·99	456	223	226	
16	9/14/48	88 ±	6·2	896 ±		341	Some gelatinous SiO_2 in spring
16	9/22/48	88 ±	6·21	896		331	
17	9/22/48	90	6·62	908		301	
18	9/16a/48	90	6·45	916		316	0930; some gelatinous SiO_2 in spring
18	9/22/48	92	6·54	908		331	Some gelatinous SiO_2 in spring
18	10/5/48	89				331	Some gelatinous SiO_2 in spring
19n	9/22/48	76	6·90	882		308	Some gelatinous SiO_2 in spring
20	9/22/48	86	6·14	872		317	
21	9/17a/48	83	6·15	888	296	293	0940; much gelatinous SiO_2 in spring
21	9/17b/48					295	1350; much gelatinous SiO_2 in spring
21	9/24/48	84·6	6·17	884	291	292	
21	9/30/48	84·2	6·62?	888	288	289	
21	10/5/48	84				297	
23	9/22/48	94	7·21	928		331	Some gelatinous SiO_2 in spring
23n	9/13/48		7·66	924		325	Small active geyser
23n	9/22/48	93	7·8	924		328	
23n	10/2/48	94	8·19	922	320	322	
24	9/13a/48	93	7·05	924		348	1430; much gelatinous SiO_2 in spring
24	9/14/48	94	7·43	932		345	
24	9/22/48	93				331	
24	10/2/48	94	7·54	920	335	335	

Table 1 (*continued*)

Spring	Date collected	Temp. °C[1]	pH[2]	Cl. p.p.m.[3]	Total SiO$_2$, p.p.m.[4]	Dissolved SiO$_2$, p.p.m.	Comments
25	9/24/48	88	7·39	892		293	
25s	9/24/48	80	7·27	890		316	
26	9/24/48	94	7·53	888		297	
26	10/2/48	96	7·97	880	273	300	
32	9/24/48	94	7·16	888		291	
33	9/13/48	54	5·87	784		210	
	9/24/48	38	5·90	724		189	
	10/2/48	35±	5·8±	700		186	
44	9/24/48	50	5·89	848		288	Some gelatinous SiO$_2$ in spring
46	9/24/48	76	5·95	856		294	
50	9/24/48	59	5·57?	848		279	Considerable gelatinous SiO$_2$ in spring
50	10/2/48	59	6·07	848		277	
Steam-boat well	9/24/48	88+	8·31	624		233	Erupting well
	10/2/48	94	8·76	668	209	219	Erupting well
South Steam-boat well	9/13/48	43	8·35	7·6		4	Warm meteoric water
Tachino-1 well	10/1/48	33	7·48	5·6	89	90	Warm meteoric water
Tachino-2 well	10/1/48	10±	7·25	5·6		74	Cold meteoric water
Damonte	10/1/48	54	6·73	532	175	182	Warm spring
Zolezzi	10/1/48	42	7·57	84	122	122	Warm spring
Bowers	10/2/48	47	9·37	7·6	45	46	Warm spring
Moana well	10/1/48	88	8·02	52	118		Hot well
	10/4/48				117	118	
	10/6/48					116	
Steam-boat Creek	9/13/48	15±	7·41	5·2		48	
Whites Creek	9/13/48	15±	7·71	2·8		10	
Steam-boat cold well	10/1/48	19	7·06	6·4	61	56	

[1] Vent temperatures.

[2] Determined by Beckman pH meter in the laboratory when sample bottle was first opened.

[3] Determined by titration with silver nitrate.

[4] Determined within two days after sample was collected. Sample heated with NaOH, and silica determined colorimetrically.

(1953). The colour intensity of the molybdate reaction is lessened by high salinity. CHOW and ROBINSON found a salt factor of 1·23 for sea water and KRAUSKOPF (1956) found that the solubility of amorphous silica in sea water was the same as in dilute water if the salt factor was applied.

As described elsewhere, total silica was determined by both gravimetric and

colorimetric methods in eight samples of Steamboat Springs water that had been aged for about three months (see Table 7). On the average, the gravimetric quantities exceed the colorimetric by about 13 p.p.m, or about 5%. A close agreement is obtained if a salt factor of 1·05 is applied to the colorimetric quantities; the solubility of silica in hot-spring waters is also in closer agreement with KRAUSKOPF's solubilities. Whether or not the discrepancies are actually explained by a salt effect is not known.

Influence of pH. ALEXANDER *et al.* (1954) and KRAUSKOPF (1956) conclude from experimental evidence that the solubility of amorphous silica is largely independent of pH within the range of about 1 to 9. The silica content of natural waters supports this conclusion. The content of all acid waters included in Tables 1 and 2 is as much or more than that of most alkaline waters. There is also no clear relation between pH and degree of supersaturation. Amorphous silica appears to be at least as soluble in acidic as in slightly alkaline water, in sharp contrast to opinions that have been held in the past by most geologists and chemists.

DEPOSITION OF SILICA ON HOT-SPRING APRONS AT STEAMBOAT SPRINGS

The behaviour of silica downstream from the spring vents was studied to clarify the roles of algae, aeration, agitation, and sinter in precipitating silica. ALLEN (1934b, p. 373–389) had stated that the silica of Yellowstone hot springs was precipitated largely by inorganic processes. To test this conclusion, samples were collected from the discharge stream of spring 21, which flowed over a prominent algal apron. The stream was then diverted to a new channel over dry opaline sinter, where algae were absent. For comparison with these samples, water from the same spring was cooled and evaporated by pouring the water back and forth from a sprinkling can to a metal bucket, in a control experiment designed to eliminate influences of algae and sinter.

Control experiments. A large sample from spring 21 was cooled and evaporated by pouring from a sprinkling can. Small samples were removed at the time-intervals shown in Table 3 and Fig. 2.

In Fig. 2 and following figures, silica is plotted against chloride, which permits a direct comparison of the curves. Chloride is merely concentrated by evaporation, undergoing no chemical change. It is therefore possible to calculate a reference curve for total silica. The difference between calculated and measured total silica is due to precipitation of gelatinous silica, assuming no analytical errors.

As the sample evaporated, soluble silica became concentrated at a rate approximately equal to that of chloride, and was not affected by the rapid lowering of temperature. Some of the samples contained 200% more silica than the saturation value with respect to amorphous silica at the temperature of collection. The difference between measured total and calculated total silica was due to formation of gelatinous silica or to analytical errors. Dissolved silica was probably identical to total silica except in the final sample, in which colloidal silica had probably started to form.

Aeration and agitation had surprisingly little influence, within the first two hours of the experiments, in polymerizing monomeric silica. Some differences were apparent in the dissolved silica content of samples aged for three days, but the ageing effects are discussed later in this paper.

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Sample	Date collected	Approx. time elapsed	Temp. °C	pH	Cl, p.p.m.	Total SiO₂, p.p.m.[1]	Dissolved SiO₂, p.p.m.[2]	SiO₂ analyst and comment
Norris, Yellowstone Green Dragon	8/27/54	90 days	87	2·47	408	496	369	H. Kramer
		305 days		2·5		419	332	K. Krauskopf
Vermillion Spring	9/28/47	0	90 ±	1·86	12		280 ± 20	D. E. White[3]
	8/25/54	90 days	90	1·97	14·5	115	109	H. Kramer
		307 days		2·1		110	110	K. Krauskopf
W. of Norris drill-hole	8/25/54	90 days	70	2·20	6·0	364	259	H. Kramer
		307 days		2·3		281	270	K. Krauskopf
Porcelain Terrace	1930 ±	? days			742	717		E. T. Allen[4]
	9/28/47	0	94 ±	8·08	748		500 ± 30	D. E. White[3]
	8/25/54	90 days	94	7·68	708		113	H. Kramer
		307 days		7·6		693	113	K. Krauskopf
Spring 200 ft SW of Pearl	9/28/47	0	91	6·47	752		450 ± 30	D. E. White[3]
	8/3/51	3 yrs	84	7·45	744	529		W. W. Brannock; colloidal SiO₂ at vent
Upper Basin, Yellowstone Daisy geyser	10/1/47	0	92 ±	7·64	302		280 ± 20	D. E. White[3]; before eruption
		0	94 ±	8·77	318		240 ± 20	D. E. White[3]; during eruption
Riverside geyser	1930 ±	? days	93·5		296	242		E. T. Allen[4]
	10/1/47	0	94·8	9·02	288		240 ± 20	D. E. White[3]

Sapphire Pool	1930±	? days	94·5		307	321		E. T. Allen[4]
	10/1/47	0	95·4	9·15	309		320 ± 20	D. E. White[3]
Midway Basin, Yellowstone Excelsior geyser	1930±	? days	91		271	237		E. T. Allen[4]
	9/30/47	0		845	278		280 ± 30	D. E. White[3]
Lower Basin, Yellowstone Ojo Caliente	1930±	? days			324	218		E. T. Allen[4]
	9/30/47	0	95·7				240 ± 30	D. E. White[3]
Mammoth, Yellowstone	1930±				162–175	29–72		E. T. Allen[4]; range of 6 springs
	9/29/47		72–73	6·5–6·6	168		50 ± 10	D. E. White[3]; two springs
	8/25/54	90 days	70·5	6·9	169		56	H. Kramer
Morgan Springs, California Growler	7/29/49	100 days	95	7·83	2427	233		W. W. Brannock
	9/7/54	75 days	96	7·42	2400		111	H. Kramer
		290 days		7·7		232	109	K. Krauskopf
Spring 6	9/7/54	75 days	96	6·64	2160	152	159	H. Kramer
		290 days		8·2		155	116	K. Krauskopf
Spring 12	9/7/54	75 days	76	6·48	2340		163	H. Kramer
		290 days		7·3		197	140	K. Krauskopf
Wilbur Springs, California	8/3/49	75 days	57	7·24	11030	190		W. W. Brannock
	3/25/54	15 mos.	53	9·2	10400	138	113	K. Krauskopf
Oil test near Wilbur	4/24/55	4 mos.	21	7·2	11000		13	H. Almond
Tuscan Springs	6/9/54	62 days	30	8·3	11800	40		H. Kramer

[1] Determined colorimetrically after conversion to the monomeric form by boiling in NaOH.
[2] Determined colorimetrically without preliminary treatment by reaction with molybdic acid.
[3] Determined colorimetrically by visual method.
[4] Gravimetric determination, Allen and Day, 1935, pp. 249, 268, 277, 373, 469.

Silica in hot-spring waters

Table 3. Silica content of samples from spring 21, Steamboat Springs, collected 30 September 1948; water cooled and evaporated by pouring from one container to another.

No. and Time	Temp. °C	pH	Cl, p.p.m.	Calculated total SiO_2, p.p.m.[1]	Measured total SiO_2, p.p.m. 9/30/48[2]	Dissolved SiO_2, p.p.m.[3]		
						9/30/48	10/3/48	1/25/49
21–1 1007	84·2	6·62	888	289	288	289	286	110[4]
21–2 1019	62	7·72	910	296	288	289	166[5]	
21–3 1032	43	8·01	926	302	298	290	160	
21–4 1053	27	8·16	944	308	299	312[6]	154	
21–5 1106	23	8·22	950	310	302	318[6]	154	
21–6 1135	17	8·27	956	312	298	318[6]	154	
21–7 1203	14	8·34	976	318	309	312	156	
21–8 1316	17	8·43	1074	350	331	312	163	

[1] Theoretical total SiO_2 as influenced by evaporation; calculated from chloride data and 9/24 SiO_2 measurements.
[2] In solution and colloidal suspension; determined colorimetrically on day of collection after boiling sample with NaOH.
[3] Determined colorimetrically by reaction with ammonium molybdate.
[4] Total SiO_2, 10/2/49, 277 p.p.m.
[5] Total SiO_2, 10/4/48, 261 p.p.m.
[6] Exceeds calculated theoretical total SiO_2, presumably due to error in determination of Cl or SiO_2.
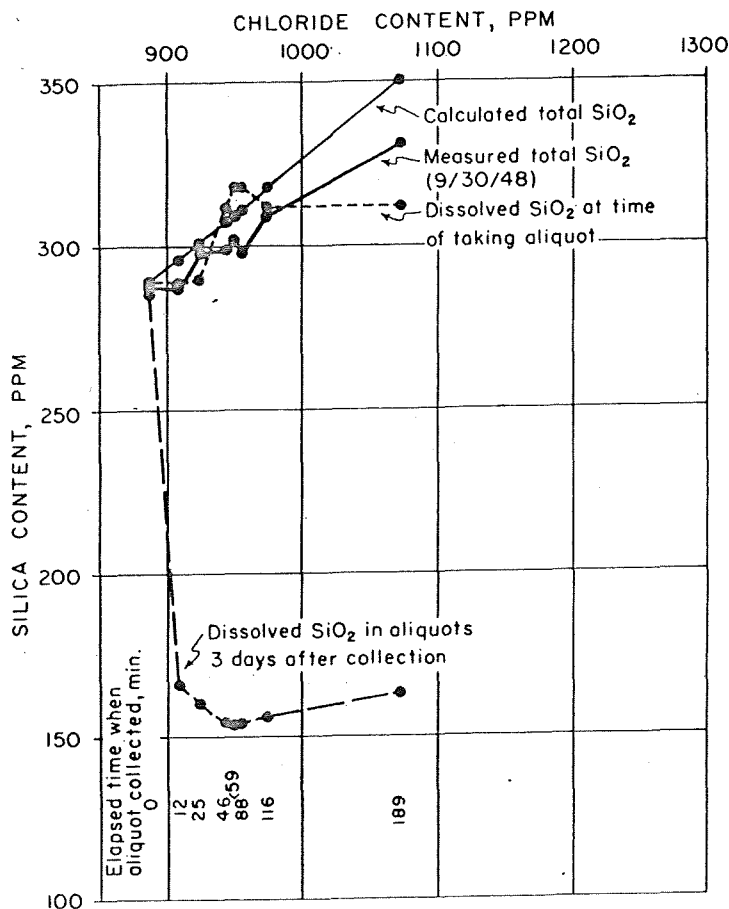

Fig. 2. Changes in the silica content of a vent sample cooled and evaporated by pouring from one container to another. Spring 21, Steamboat Springs, 30 September 1948.

Table 4. Silica content of samples from spring 21, Steamboat Springs, collected 24 September 1948, from discharge stream diverted to a new channel without algae.

Distance from vent, ft	Temp. °C	pH	Cl, p.p.m.	Calculated total SiO$_2$, p.p.m.[1]	Measured total SiO$_2$, p.p.m. 9/26/48[2]	Dissolved SiO$_2$, p.p.m.[3]			
						9/24	9/25	9/26	Feb. 10±, 1949
0	84·6	6·17	884	292	291	292	292	289	108
50	63	7·11	908	300		286			
100	47	7·61	936	309	302	286	292(?)	157	
150	27	7·73	980	322		280			
200	24	7·79	1000	330	276	259	197	161	
300	18	7·90	1040	345	255	246	212	169	
400	12	7·96	1080	357	224	212	223	193	

[1] Theoretical total SiO$_2$ as influenced by evaporation; calculated from chloride data and 9/24 SiO$_2$ measurements.

[2] In solution and colloidal suspension; determined colorimetrically two days after collection by boiling sample in NaOH.

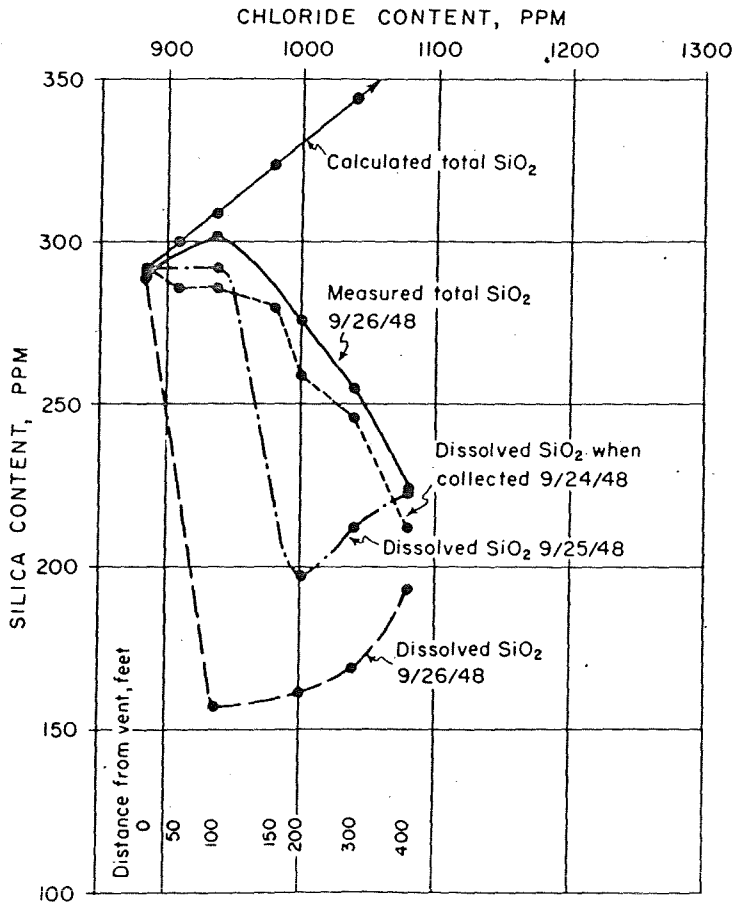[3] Determined colorimetrically by reaction with ammonium molybdate.

Fig. 3. Samples from a new discharge channel without algae. Spring 21, Steamboat Springs, 24 September 1948.

Table 5. Silica content of samples from spring 21, Steamboat Springs, collected 17 September 1948, from discharge stream running over an established algal colony.

Distance from vent, ft	Temp. °C	pH	Cl, p.p.m.	Calculated total SiO₂, p.p.m.[1]	Measured total SiO₂, p.p.m. 9/19/48[2]	Dissolved SiO₂, p.p.m.[3]			
						9/17	9/18	9/25	1/24/49
0	83	6·15	888	293	287	293	289	195	114
50	63	7·29	914	301	294	295	254	134	
100	38	7·73	952	314	291	293	199	130	
150	33	7·80	964	318	288	285	211	129	
200	21	7·97	994	328	216	223	221	186	
500	17	8·14	1064	351	196	197	204	199	
800	18	8·81	1936	639	70[4]	72	72	75	

[1] Theoretical total SiO₂ as influenced by evaporation; calculated from chloride data and 9/17 SiO₂ measurements.
[2] In solution and colloidal suspension; determined colorimetrically two days after collection by boiling sample with NaOH.
[3] Determined colorimetrically by reaction with ammonium molybdate.
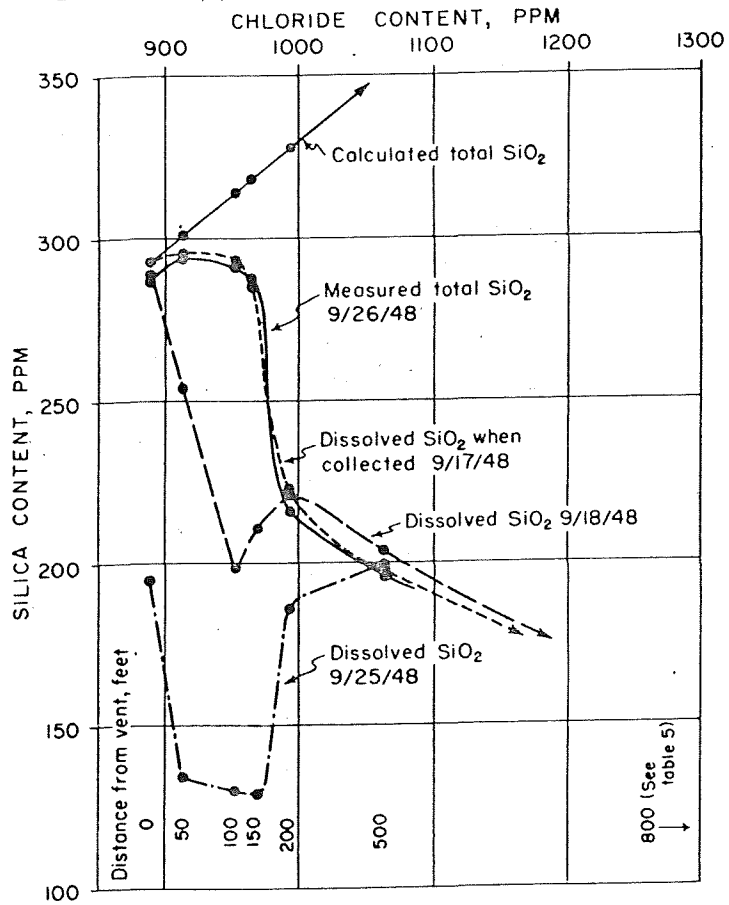[4] Determined 20/9/48.

Fig. 4. Samples from an old discharge channel with abundant algae. Spring 21, Steamboat Springs, 17 September 1948.

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Sinter channel without algae. The measurements of 24 September 1948, when the discharge stream of spring 21 was diverted to a new channel without established algae, are shown in Table 4 and Fig. 3. Measured total silica at first increased with chloride as a result of evaporation, as in the control experiment described above, but some polymerization of dissolved silica started to occur immediately downstream from the vent. Colloidal silica remained in suspension in significant quantity, but began to precipitate about 100 ft from the vent, at least in part as gelatinous silica that was actually observed in the lower part of the channel.

The behaviour of dissolved silica was very different from that in the control experiment. The degree of supersaturation became high, but not nearly as high as in the control samples. The extent of agitation and aeration was probably similar for the two series of samples. The most obvious difference was the fact that the water of the 24 September series was in direct contact with previously deposited opaline sinter.

Normal channels with sinter and algae. Table 5 and Fig. 4 demonstrate the behaviour of silica in water on a normal spring apron. At Steamboat Springs, algae flourish in particular at temperatures between 30 and 60°C. They have been observed in water as hot as 69 or 70°C, but because of daily and seasonal fluctuations they are not conspicuous at temperatures above 65°C.

When the samples in Table 4 were obtained, spring 21 flowed over a well developed algal colony extending from about 50 to 240 ft below the vent and ranging up to 10 ft in width. Nearer the vent, the water was too hot, and at greater distances diurnal fluctuations in temperature were probably too great for algae to flourish.

For the first four samples, the curve for dissolved silica is similar to that of Fig. 3, but from 150 to 200 ft below the vent, dissolved (monomeric) silica was polymerized more rapidly than where algae were absent.

Table 6 and Fig. 5 contain the results of a similar study on spring 18, which flowed over a normal algal apron extending from about 25 to 150 ft below the vent. Conditions were similar to those of spring 21 when flowing over an algal apron, but the results were more nearly comparable to those of spring 21 when flowing in a new channel without algae. For the four series of measurements, dissolved silica attained a maximum of 376% of the equilibrium amount (about 83 p.p.m. at 14°C, according to Fig. 1) in sample 7 of the control series (see Table 3). Corresponding figures for the other series are: Spring 21 on sinter without algae, 272% of the equilibrium amount of 78 p.p.m. at 12°C at 400 ft; spring 21 on sinter and algae, 223% of the equilibrium amount of 100 p.p.m. at 21°C at 200 ft; spring 18 on sinter and algae, 315% of the equilibrium amount of 100 p.p.m. at 21°C at 75 ft. The measurements on spring 21 suggest that algae were somewhat effective in increasing the rates of polymerization and precipitation of silica, but this conclusion is not clearly supported by measurements on spring 18.

The evidence is clear that algae are, at best, only a minor factor in causing polymerization and precipitation of silica at Steamboat Springs. Contact with sinter, on the other hand, is definitely a major influence in inducing both polymerization, as indicated by the decrease in dissolved (monomeric) silica, and

Table 6. Silica content of samples from spring 18, Steamboat Springs, collected 16 September 1948 from discharge stream running over an established algal colony.

Distance from vent, ft	Temp. °C	pH	Cl, p.p.m.	Calculated total SiO$_2$, p.p.m.[1]	Measured total SiO$_2$, p.p.m.[2]	Dissolved SiO$_2$, p.p.m.[3]			
						9/16	9/17	9/18	9/25
0	90	6·45	916	315	323	315	229	170	130
50	39	7·84	984	339	338	331	167	148	123
75	21	8·01	1020	351	331	315		150	127
100	17	7·98	1028	354	297	279	170	161	131
200	13	8·00	1128	388	244	241	223	211	140
400	7	8·02	1220	420	179	176	170	180	180

[1] Theoretical total SiO$_2$ as influenced by evaporation; calculated from chloride data and 9/16 SiO$_2$ measurements.

[2] In solution and colloidal suspension; determined colorimetrically three days after collection by boiling sample with NaOH.

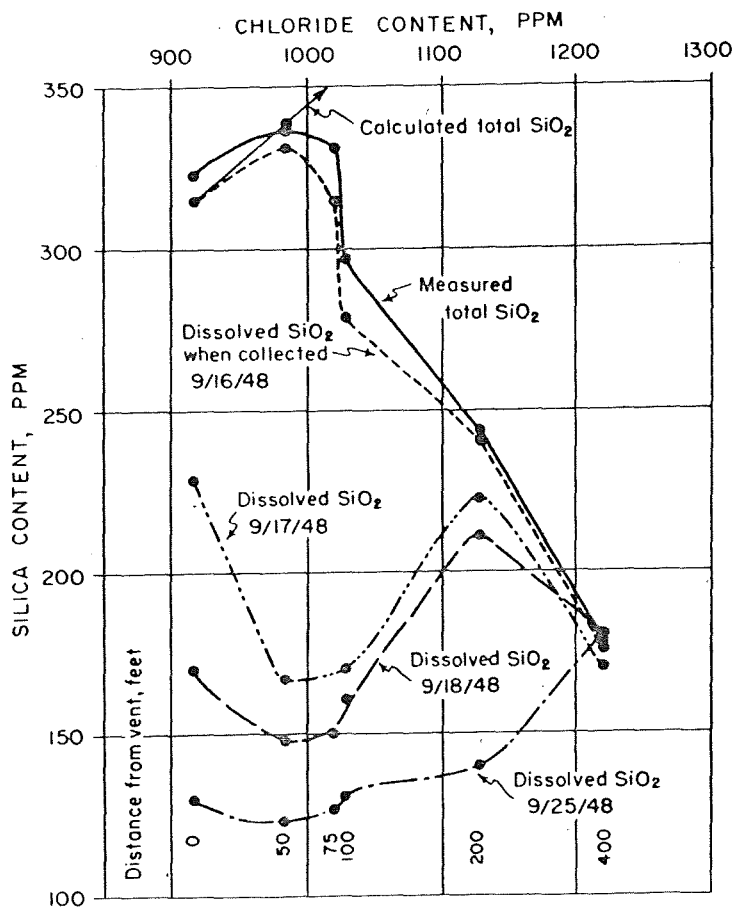[3] Determined colorimetrically by reaction with ammonium molybdate.

Fig. 5. Samples from an old discharge channel with abundant algae. Spring 18, Steamboat Springs, 16 September 1948.

precipitation, as indicated by the decrease in total silica. This conclusion is supported by data from samples that were aged in contact with sinter.

SILICA IN AGED SAMPLES

Polymerization of soluble silica. Many samples from the Steamboat Springs area were aged at room temperature in stoppered bottles with plastic linings in order to determine rates of polymerization and precipitation (see Table 7). In most
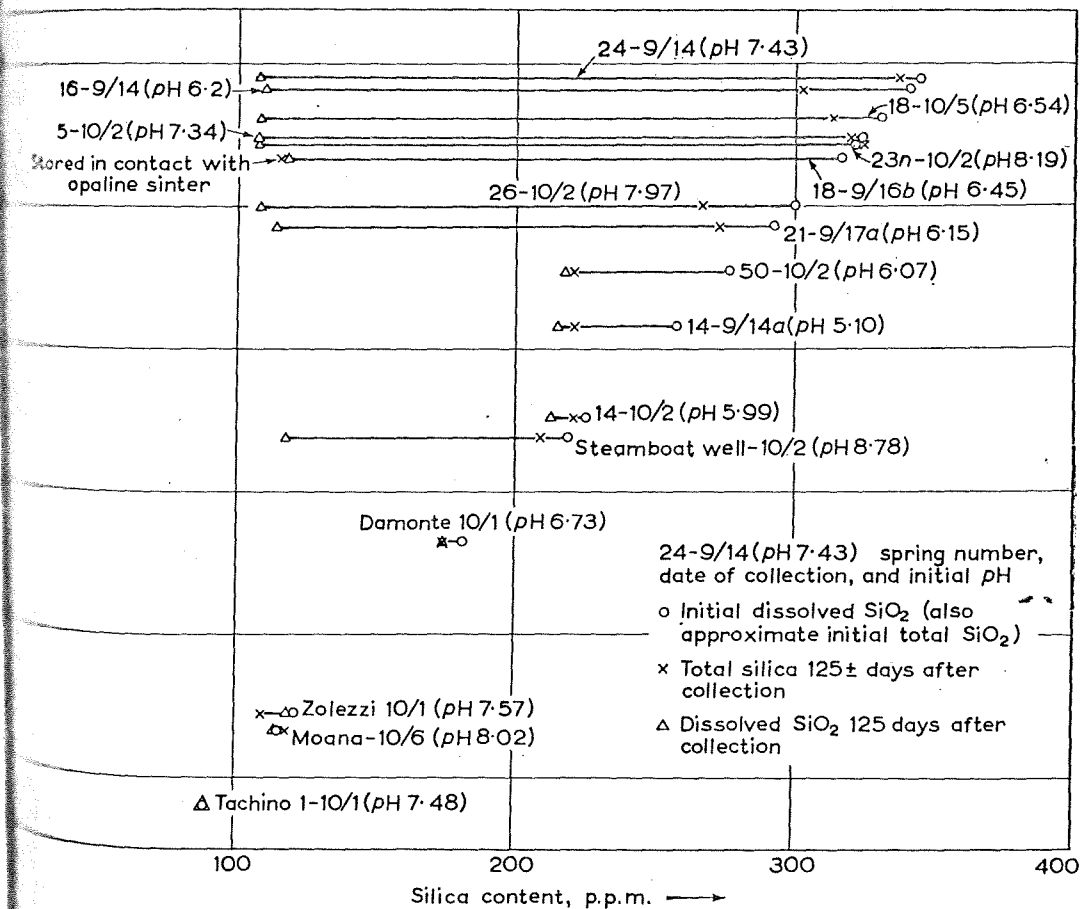

Fig. 6. Net changes in the content of dissolved and total silica in thermal waters of the Steamboat Springs area during four months after time of collection.

samples, with time, some dissolved silica polymerized to colloidal silica, and at still lower rates some colloidal silica precipitated as gelatinous silica.

Fig. 6 shows the net changes that occurred in the 4 months following the time of collection. In most samples soluble silica decreased to about 110 p.p.m., and a small part of the newly-formed colloidal silica precipitated as gelatinous silica.

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Rates of polymerization of some representative samples are shown in Fig. 7. Some waters initially highest in dissolved silica polymerized extensively within twenty-four hours, but others with an intermediate content showed no significant change in four months. Sample 24-9/13a was polymerizing very rapidly twenty-four hours after collection. A similarly rapid change in sample 21-9/24, however, did not occur until at least the fifth day.
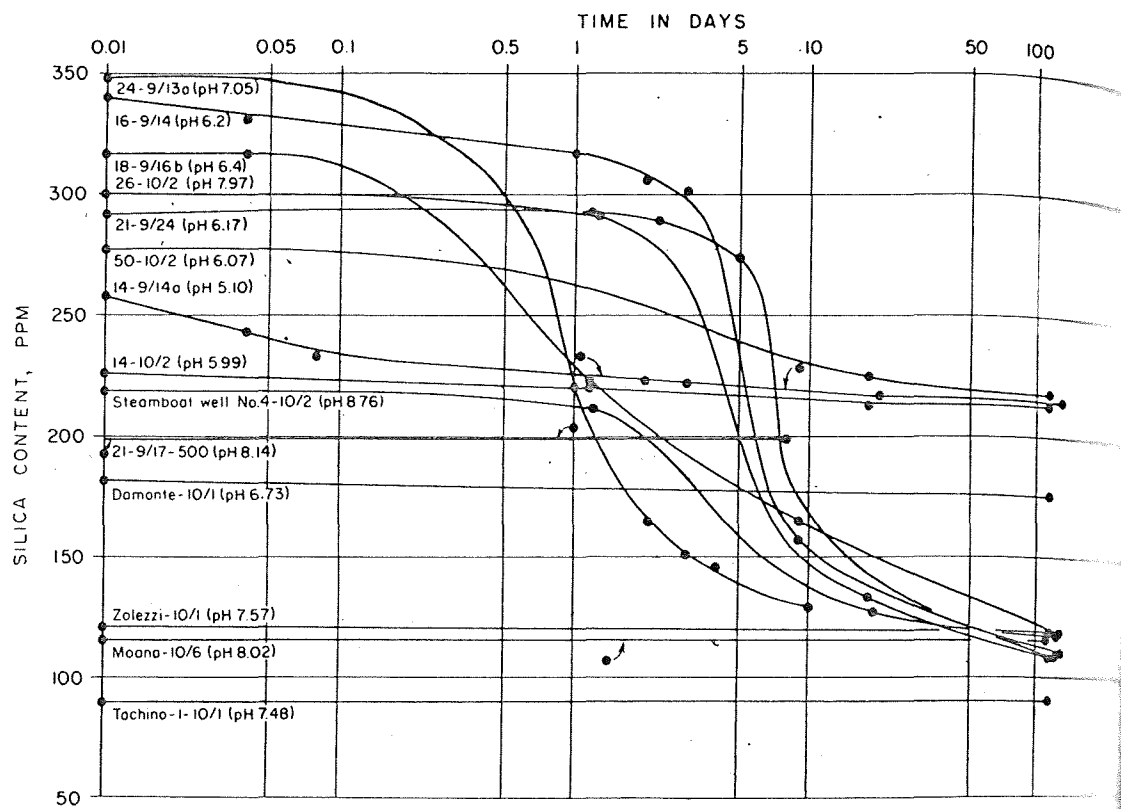

Fig. 7. Changes in content of dissolved silica with time in some representative samples from the Steamboat Springs area.

Krauskopf (1956) has shown that rate of polymerization is most rapid at high pH and high salinity. Evidence from hot springs suggests that the degree of supersaturation, the presence of previously-formed colloidal particles, and the nature of foreign substances also influence the rate of polymerization. These factors are discussed in the following paragraphs.

Equilibrium in neutral and alkaline waters. The content of dissolved silica in alkaline vent samples decreased with time when stored at room temperature, eventually attaining approximate equilibrium at 106 to 118 p.p.m. Fifteen of nineteen samples in Table 7 with initial silica above 118 p.p.m. and pH's above

attained this range within four months. The average of the fifteen samples is 110 p.p.m. of dissolved silica. This is very close to the content of dissolved silica of a sample from spring 27 that had aged at room temperature for more than nine years (Table 7), suggesting that four months is sufficient for most neutral and alkaline waters to reach equilibrium. The exceptions are discussed separately.

Fig. 6 shows the relationships between initial and final total silica in samples that had aged about 125 days. The difference between these two quantities is precipitated or gelatinous silica. Most samples that showed a significant decrease in dissolved silica also showed a decrease in total silica of a smaller magnitude. In the alkaline samples, most of the polymerized silica remained in suspension as colloidal particles, but there were a few samples in which as much as 20% flocculated.

Metastability of acid waters. The three most acid waters of Table 7 and Fig. 7, samples 50-10/2, 14-9/14a, and 14-10/2, ranged in pH from 5·10 to 6·07. The content of dissolved silica did not fall below 220 p.p.m. in 125 days when stored at room temperature. These waters, however, were also lower in silica than most Steamboat samples, and were therefore not as strongly supersaturated. Slightly to moderately supersaturated waters, as will be seen, do not attain equilibrium as rapidly as waters that are highly supersaturated. Effects of pH and degree of supersaturation could not be distinguished clearly in the acid Steamboat samples.

Two strongly acid springs from the Norris Basin of Yellowstone Park contained 496 and 364 p.p.m. of total silica ninety days after collection (see Table 2). When the samples were first collected, dissolved silica was probably at least as high as the total silica found ninety days later. Even though the samples were aged for more than ten months, they did not reach the equilibrium attained by most alkaline samples in four months.

The difference in origin between the high- and low-chloride acid springs should be noted. The latter, called acid-sulphate springs, consist of steam condensed near the ground surface and mixed with rain and snow-water (WHITE, SANDBERG, and BRANNOCK, 1953, p. 493). The acidity is caused by surface oxidation of H_2S. Silica is dissolved from the immediate borders of the spring pools, and, depending on precipitation and rate of discharge, may show a wide range in concentration from time to time, as indicated by the two analyses of Vermillion Spring (Table 2). The acidity of springs high in chloride, called acid-chloride springs, is of less certain origin (WHITE, 1955, pp. 106–7). Some springs, including the Green Dragon (Table 2), are relatively high in discharge. Chloride and silica are transported upward in solution from depths where temperatures are much higher than the surface boiling-point. Because of this difference in origin, acid-chloride springs may be supersaturated with respect to amorphous silica at vent temperatures because of the rapid drop in temperature near the surface, but acid-sulphate springs are commonly unsaturated.

ILER (1955, p. 46) and KRAUSKOPF (1956) have shown that equilibrium with dissolved silica is attained much more slowly at low pH than at high pH. Data from hot springs are for the most part consistent with this conclusion. Equilibrium

Table 7. The effect of ageing on the silica content of water samples from the Steamboat Springs area. Italicized quantities were determined gravimetrically.

Spring	Date collected	Time elapsed[1]	Temp °C	pH	Cl p.p.m.	Total SiO_2, p.p.m[2]	Dissolved SiO_2, p.p.m.[3]	Comments
5	10/2/48	0	95	7·34	926		324	
		28 h				330	308	
		18 d					134	
		114				304	107	
						320		
14	9/14a/48	0	80 ±	5·10	566		258	
		1 h					243	
		2 h					233	
		25 h					233	
		2 d					223	
		3 d				226	222	
		9 d					228	
		20 d					217	
		132 d				221	215	
14	9/14b/48	20	80 ±	5·10	566	220	218	Rubber bottle.
14	10/2/48	0	92	5·99	456		226	
		28 h				223	220	
		18 d					213	
		114 d				*221*	213	
16	9/14/48	0	88 ±	6·2	896 ±		341	Some gelatinous SiO_2 in spring
		1 h					331	
		24 h					317	
		2 d					306	
		3 d				312	302	
		9 d					157	
		132 d				302	110	
18	9/16a/48	0	90	6·45	916		316	0930; some gelatinous SiO_2 in spring
		5 h					316	
		6 h					316	
		7 h					316	
		29 h					229	
		54 h					170	
		3 d				323		
		9 d					130	
18	9/16b/48	0					317	1540; cooled and bottled in contact with sinter fragments.
		1 h					317	
		27 h					224	
		9 d					165	
		130 d				115	118	
18	10/5/48	0	89				331	
		112d				300	108	
						313		

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Table 7 (*continued*).

Spring	Date collected	Time elapsed[1]	Temp. °C.	pH	Cl, p.p.m.	Total SiO$_2$ p.p.m.[2]	Dissolved SiO$_2$ p.p.m.[3]	Comments
18	1/5/50a	112 d	77·7	6·90	908	303	116	Control sample for following.
18	1/5/50b	112 d	77·7			161	120	Opaline sinter added.
18	1/5/50c	112 d	77·7			221	168	Chalcedonic sinter added.
18	1/5/50d	112 d	77·7			280	114	Calcite added.
21	9/17a/48	0	83	6·15	888		293	0940; much gelatinous SiO$_2$ in spring
		3 h					286	
		1 d				296	289	
		8 d				287	195	
		129 d				273	114	
21	9/24/48	0	84·6	6·17	884		292	
		28 h					292	
		54 h				291	289	
		5 d					274	
		122 d					108	
21	9/30/48	0	84·2	6·62	888	288	289	
		3 d					286	
		117 d				277	110	
21	10/5/48	0	84	6·7			297	
		112 d				268	112	
						281		
23n	10/2/48	0	94	8·19	922		322	
		1 d				320	227	
		18 d					126	
		115 d				298	107	
						325		
24	9/13a/48	0	93	7·05	924		348	1430; much gelatinous SiO$_2$ in spring
		24 h					220	
		50 h					164	
		3 d					151	
		4 d				342	146	
		10 d					128	
24	9/13b/48	19 d				333	130	1750; rubber bottle.
		20 d				335		
24	9/14/48	0	94	7·43	932		345	
		31 h					178	
		54 h					155	
		3 d				346	150	
		9 d					129	
		18 d					130	
		132 d				337	108	

Table 7 (continued).

Spring	Date collected	Time elapsed[1]	Temp. °C	pH	Cl, p.p.m.	Total SiO2 p.p.m[2]	Dissolved SiO2 p.p.m.[3]	Comments
24	10/2/48	0	94	7·54	920		335	
		1 d				335	277	
		18 d					126	
		115 d				311	106	
						336		
27	7/30/45	0	96	7·2 ±	949	*317*		
27	1/14/46	0	94	6·76	910			
		9½ y		7·6		300	106	SiO2 by K. B. Krauskopf.
		9¾ y		8·4		319	116	SiO2 by P. Scott & W. W. Brannock 9 p.p.m. of gelatinous SiO2, not included in total
50	10/2/48	0	59	6·07	848		277	
		1 d					263	
		18 d					225	
		115 d				221	218	
						220		
Steamboat Well	10/2/48	0	94	8·76	668		219	Erupting well
		24 h				209		
		29 h				202	212	
		19 d					127	
		128 d				208	118	
						209		
Tachino–1	10/1/48	0	33	7·48	5·6	89	90	Warm well
		116 d				90	91	
Damonte	10/1/48	0	54	6·73	532		182	Warm spring
		2 d				175		
		116 d				176	176	
Zolezzi	10/1/48	0	42	7·57	84		122	Warm spring
		2 d				122		
		116 d				110	119	
Moana well	10/1/48	0	88	8·02	52		163(?)	Hot artesian well
		1 d				118	117	
		3 d				117	118	
	10/6/48	0					116	
		14 d					107	
		111 d				114	118	
"Poison" Spring	6/12/52	1½ y	20 ±	2·45	6·0		98	Non thermal area, Virginia Range
Steamboat cold spring	9/4/54	90 ± d	15 ±	6·93	4·5	57	65	Analyst, H. Kramer

[1] Elapsed time when dissolved SiO2 determined; nearest interval for total SiO2.
[2] In solution and colloidal suspension; determined colorimetrically after boiling sample and acid except italicized values, which are gravimetric.
[3] Determined colorimetrically by reaction with ammonium molybdate.

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solubility is either almost independent of pH between the range of 1 and nearly 9 or amorphous silica is more soluble in acid than in alkaline waters. Supersaturation apparently persists almost indefinitely in acid waters that are high in dissolved silica.

The slightly acid samples from springs 14 and 50 and from Damonte spring decreased only a little in dissolved silica, but colloidal silica apparently flocculated very soon after polymerization. The same relationship probably holds true for the Green Dragon and the Norris drill-hole pool of Norris Basin, Yellowstone Park (see Table 2), as indicated by the decrease in total silica.

Influence of salinity. KRAUSKOPF (1956) has shown that rates of polymerization and flocculation are increased with increasing salinity. Because time-change studies were not made in detail on hot-spring waters that differed much in salinity, this observation cannot be tested rigorously by the hot-spring data. The flocculation of colloidal silica in the Wilbur Springs sample (see Table 2), which is about ten times as high as that in the Steamboat waters, may be a result of its high concentration of electrolytes, though other samples are needed to confirm this suggestion.

Influence of degree of supersaturation. Sample 24-9/13a (Table 7 and Fig. 7) was more than 200% supersaturated with dissolved silica after cooling to room temperature. Within twenty-four hours about half of the excess silica had polymerized. Damonte spring, only slightly lower in pH but only 50% supersaturated with silica at room temperature, showed no significant polymerization in four months. Vent samples from springs 14 and 50 also showed little change, but this could be caused by low pH as well as by low degree of supersaturation.

The influence of degree of supersaturation is particularly well shown in the ageing of downstream samples (Figs. 3, 4, and 5), all of which are alkaline. The data of Fig. 5 and Table 6 have been replotted in Fig. 8. Initial rates of polymerization are clearly related to initial content of dissolved silica. Sample 18-400, for example, was only about 60% supersaturated with amorphous silica at room temperature, and was the only sample of the series that showed no significant change in nine days. It was also the highest in pH and salinity, both of which should otherwise favour polymerization. This suggests that degree of supersaturation more than outweighs the other factors in some circumstances.

No previous experimental evidence had demonstrated the significance of the degree of supersaturation. After the hot-spring work had demonstrated persistent metastability of dissolved silica in solutions less than 100% supersaturated, KRAUSKOPF (1956) confirmed the effect in laboratory experiments.

The dissolved silica of a supersaturated solution is polymerized on to spontaneously formed or pre-existing nuclei of amorphous silica. The rate of polymerization is a direct function of the number of nuclei per unit volume, each nucleus serving as a site of deposition. Solutions devoid of pre-existing nuclei show an initial induction period of nucleation which is discussed in the following section. The number of nuclei formed per unit volume and unit time is strongly dependent on the degree of supersaturation (OVERBEEK, 1952, p. 64). Thus, in the absence of an appreciable number of pre-existing nuclei, solutions of highest degree of supersaturation would form the greatest number of nuclei and polymerize at the highest rate. Solutions of lower supersaturation like samples 18-200 and 18-400,

16 September 1948 (see Table 6 and Fig. 8), contain much smaller numbers of nuclei, both pre-existing and newly formed, and consequently polymerize much more slowly.

Solutions only moderately supersaturated with respect to amorphous silica involve an additional factor of the solubility of amorphous silica being dependent on particle size in the range of the smallest particles (Iler, 1955, p. 11). Particles
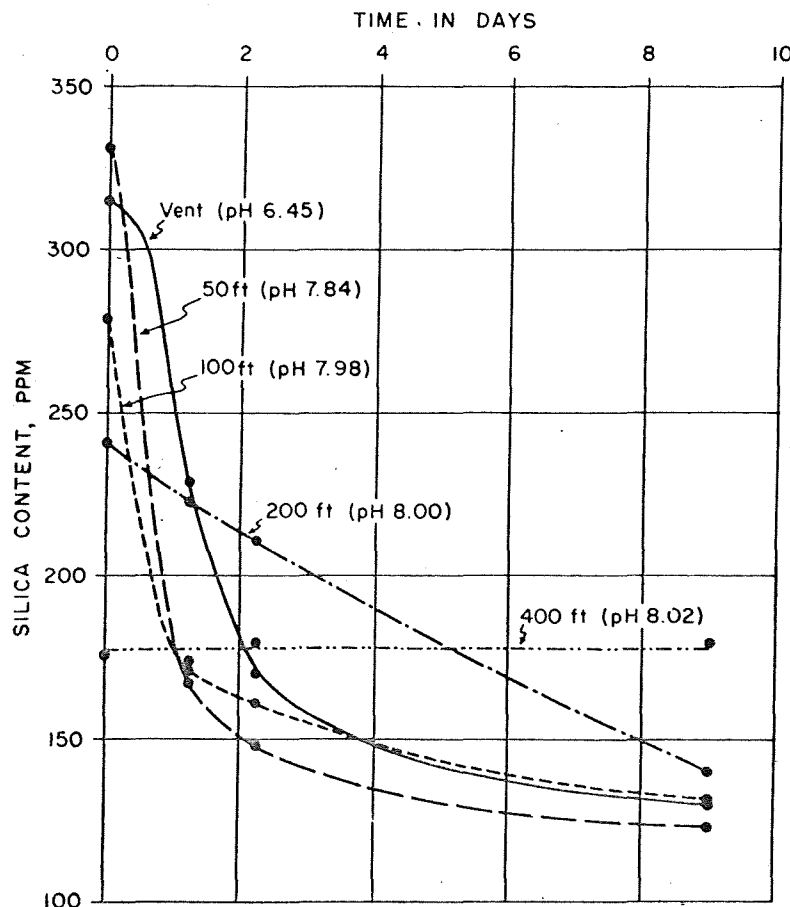

Fig. 8. Changes in the content of dissolved silica in vent and downstream samples of spring 18, Steamboat Springs, with time.

with diameters less than about 10 millimicrons have several-fold higher solubility compared to larger particles. Thus nuclei formation may be impossible in solutions of only moderate supersaturation with respect to macroscopic amorphous silica, and the rate of polymerization on to a few pre-existing nuclei that might be present may be imperceptible.

Influence of existing polymeric molecules. The vent samples of Figs. 2 to 5 all showed slower initial rates of polymerization than samples from which some silica had precipitated prior to collection. See, for example, Fig. 8, in which data from spring 18, Fig. 5, are shown in a different way. A certain interval of time is

necessary for polymerization to attain a maximum rate in the vent samples, in which all silica is present in the dissolved (monomeric) form. Downstream samples, as previously shown, generally contain some colloidal silica, and these samples polymerize more rapidly after collection than the vent samples. Initial rates of cooling of the samples may have played a minor role, but the data are more consistent with the theory that at high degrees of supersaturation "seed crystals" or centres of nucleation are formed relatively rapidly in alkaline solutions, but not instantaneously.

Influence of introduced substances. Sample 18-9/16b (see Table 7 and Fig. 6) was bottled with a small handful of porous fragments of opaline sinter a few hours after sample 18-9/16a had been collected in the normal manner. The sample containing sinter changed in dissolved silica at about the same rate as the control sample, but all polymerized silica precipitated, either as gelatinous silica or as opal. Most of the polymerized silica of other neutral and alkaline samples remained in colloidal suspension.

In the hope of clarifying this difference in behaviour, a suite of four samples was collected from spring 18 on 5 January 1950 (see Table 7). The total and dissolved silica could not be determined at the time of collection, but both concentrations were probably from 310 to 330 p.p.m. The control sample behaved as expected, attaining an equilibrium value of 116 p.p.m. of dissolved silica in 112 days.

Sample d, containing 20 g of powdered optical calcite in about 375 ml of water, was similar to the control sample in its content of dissolved silica after 112 days, but the calcite was effective in precipitating more than 10% of the colloidal silica.

Sample b, containing an equal amount of powdered opaline sinter, was very similar to sample 18-9/16b/48 with opaline sinter, except that 20% of the polymerized silica was still in suspension as colloidal silica.

Sample c contained 20 g of powdered chalcedonic sinter and a little fine-grained quartz, but no opal. This sinter precipitated more than half of the polymerized silica that formed, and was at least 50% as effective as opaline sinter in this regard. The rate of polymerization, however, was much slower than in the other three samples, failing to reach equilibrium in nearly four months. The supersaturated solution was actually partially stabilized, in contrast to expected results. In view of the fact that the solubility of quartz is only a few p.p.m. at room temperature, sample c is enormously supersaturated in relation to the solid phase with which it is in contact. The behaviour of this sample points to the need for much more study of the influence of quartz and other minerals on dissolved and colloidal silica.

The effect of opal in increasing rates of polymerization and flocculation is supported by KRAUSKOPF's experimental evidence (1956, Table 2) for a similar effect by silica gel.

NOTABLE UNSATURATED THERMAL WATERS

Some Steamboat waters. A sample demanding special comment is the final one of Table 5 and Fig. 4, collected 800 ft from the vent of spring 21. This sample contained only 72 p.p.m. of dissolved silica when collected, although the water below the vent was highly supersaturated. Its silica content was significantly less than the equilibrium quantity of about 90 p.p.m. at 18°C, the temperature of

collection (see Fig. 1), and the pool from which it was collected contained gelatinous silica. Activity of diatoms and relatively high salinity of the sample may be contributing factors, but the behaviour of the silica is definitely anomalous. A salt factor such as discussed by Chow and Robinson (1953), would have to be unreasonably large for the observed salinity to account for the difference.

Some of the values for spring samples shown on Fig. 1 lie below the solubility curve. Were these waters never higher in silica, even at depths where temperatures were much higher, or has sufficient silica precipitated as chalcedony or quartz, which is the most stable phase, for the water to be unsaturated with respect to amorphous silica? The rate of movement through subsurface channels and the rate of decrease in temperature probably differ greatly from spring to spring. High rates should favour supersaturation at vent temperatures, and very slow rates should favour unsaturation with respect to amorphous silica.

Meteoric springs. Some thermal springs appear to consist entirely of meteoric water that has circulated to considerable depth where the geothermal gradient is "normal," or that acquires its heat by conduction from a volcanic source, without volcanic water or mineral matter (White et al., 1953, pp. 491, 492.) Silica in such water is derived from weathering or from alteration and solution of rocks through which the water migrated.

Of the thermal waters of Table 1 and Fig. 1, Bowers hot spring, with 46 p.p.m. of dissolved silica, and the South Steamboat well (see White and Brannock, 1950, pp. 569–572), with only 4 p.p.m. of dissolved silica, are believed to be meteoric in origin with no more than traces of other water. Moana well (Table 1 and Fig. 1), with 118 p.p.m. of dissolved silica, is relatively high in temperature and contains a little more chloride, fluoride, and boron than normal ground water, and may have a very small amount of volcanic water. All of these waters were notably low in silica relative to their vent temperatures, and were considerably below saturation with respect to amorphous silica when collected. All springs except the South Steamboat well, however, have more silica than normal streams of the area (see Steamboat and Galena Creeks, Table 1). Some silica is dissolved by ground water, but generally in less than saturation amounts with respect to amorphous silica, except where the water is acid and rock decomposition rapid.

The silica content of the South Steamboat well is extraordinarily low, and has been determined to be 4 to 5 p.p.m. by gravimetric as well as by colorimetric methods. The water is believed to be derived from Steamboat or Galena Creek, entering alluvium a mile or more upstream from the well. All stream waters of the region that have been analysed contain at least 10 p.p.m. of silica, and the average of the surface waters is probably about 30 p.p.m. All are considerably below saturation with respect to amorphous silica, and when heated during migration to the South Steamboat well, they should become even more unsaturated. Instead of dissolving silica, however, the water of this well appears to have precipitated most of its original silica.

It is possible that, with mild heating, quartz or chalcedony is being precipitated, and that dissolved silica trends towards an equilibrium with these low-solubility minerals rather than with opal or other forms of amorphous silica

Why, then, do other heated ground waters such as Bowers hot spring contain as much or more silica than the surface streams? Ground waters may normally deposit some silica as chalcedony cement or as overgrowths on quartz, but contemporaneous chemical weathering or alteration of silicate minerals may supply as much or more soluble silica than the amount deposited. Renewal of supply may be lacking for the water of the South Steamboat well, perhaps because the water is sufficiently high in temperature to precipitate chalcedony but is too high in pH, without enough free CO_2 to attack silicate minerals. Although the relationships are not clear, this water is of special interest because its silica content definitely trends away from the equilibrium indicated by other thermal waters.

Calcium bicarbonate springs. Thermal springs of the calcium-bicarbonate type have been discussed by ALLEN (1934a, pp. 345–349), ALLEN and DAY (1935, pp. 360–376), and WHITE, SANDBERG, and BRANNOCK (1953, p. 493). This type of water deposits calcium carbonate, and differs from the sinter-depositing alkali-bicarbonate-chloride waters of the Yellowstone geyser basins and Steamboat Springs. Travertine-depositing springs are probably always associated with sedimentary rocks and no doubt owe their characteristic features to solution of limestone at depth. Large volumes of meteoric water may mix at relatively low temperature, permitting relatively high concentrations of dissolved calcium bicarbonate. As ALLEN and DAY (1935, p. 375) have pointed out, Norris Basin water contains abundant free CO_2 and, upon contact with limestone, should dissolve $CaCO_3$ (if temperatures are sufficiently low) and should change to the calcium-bicarbonate type. These authors, however, did not explain the silica relations of the two types of water.

All travertine-depositing waters are notably low in silica, seldom containing more than 50 or 60 p.p.m., which is within the range of normal cold ground-water, but is far below that of other volcanic thermal waters not in contact with limestone. Fig. 1 indicates that Mammoth water at its vent temperature and with 50 to 56 p.p.m. of dissolved silica is farther from saturation with respect to amorphous silica than any other analysed thermal water. If the volcanic component of the Mammoth water was as high in silica at depth as that of the major geyser basins, much silica has actually been precipitated. It appears that, in contact with limestone, silica may precipitate while calcium carbonate dissolves. Silicification of limestone is geologically an attractive possibility, but if this occurs at depth, the silica content of the water is trending away from saturation with amorphous silica and towards equilibrium with quartz or chalcedony. The effect of calcium magnesium, and CO_2 on the solubility of the different forms of silica, and on rates of precipitation, deserves further study.

Connate springs and oilfield brines. Tuscan springs (see Table 2) and the water of an oil-test well one mile south-east of Wilbur springs (included in Table 2, even though not a thermal spring) are believed to be typical of many connate waters. Most oilfield brines contain from 20 to 60 p.p.m. of total silica (see, for example, MEENTS *et al.*, 1952, pp. 22–37; CLARKE, 1924, pp. 184–185), which is far below saturation with amorphous silica, probably because the waters are trending toward equilibrium with quartz and chalcedony.

Wilbur Springs (Table 2), Colusa County, California, are believed to consist

of connate water that rises through serpentine and pre-Cretaceous rocks. Its content of total silica, 190 p.p.m., indicates probable saturation with amorphous silica at the vent temperature, particularly in view of the fact that no salt factor has been applied. The high silica content may result from extensive alteration at depth, or may reflect high solubility of olivine or serpentine through which the water has probably flowed.

The only other connate water reported to lie near the saturation curve for amorphous silica was found by Emery and Rittenberg (1952, p. 746), who determined the silica content of pore water by colorimetric methods in recent ocean-basin sediments (pp. 743–752). Approximate temperatures *in situ* are also indicated (p. 739). Most of the pore waters are approximately 50% saturated with dissolved silica but those of the Santa Cruz Basin (p. 746) contain as much as 68 p.p.m. (without a salt factor) which, at 4°C, is on Krauskopf's solubility curve for dilute water (Fig. 1) and is a little above the curve for sea water.

Ocean water after burial in sediments is out of contact with silica-secreting organisms such as diatoms, radiolaria, and siliceous sponges. If the sediments contain a sufficient quantity of the opaline hard parts of these organisms, and if quartz, chalcedony, and authigenic silicate minerals are not formed too rapidly, the water should in time become saturated with respect to amorphous silica. After the supply of amorphous silica is eventually converted to more stable silica minerals, the silica content of connate water should in time come to equilibrium with quartz.

The lack of saturation with amorphous silica for most connate waters, and also for old ground-waters, cannot be ascribed to lack of time nor, as far as known, to the activity of silica-secreting organisms. The more probable reason for the low silica content of these old waters is that equilibrium is gradually being attained with respect to quartz, which is the stable form of silica at low temperature, with a solubility of only a few parts per million. In a water unsaturated with respect to amorphous silica, opaline organic remains should dissolve. The same water is supersaturated with respect to quartz or chalcedony, and these minerals should precipitate. At low temperatures, however, the rates of precipitation of quartz and chalcedony may be exceedingly slow.

Hot waters with high CO_2 content attack susceptible silicate minerals, with monomeric silica as a probable by-product. Oxidation of some silicate minerals may also provide monomeric silica. At some stages in the history of certain ground waters, the content of dissolved silica may increase; after the content of CO_2 and oxygen is exhausted, the content of dissolved silica may trend downward toward equilibrium with respect to quartz and chalcedony.

Origin of the Silica Minerals

General remarks. Gelatinous silica is the most soluble form of silica, and its solubility at different temperatures is now known within narrow limits. Solutions saturated with respect to gelatinous silica are supersaturated with respect to quartz, cristobalite, and other polymorphs, and this supersaturation may be exceedingly high. The degree of saturation of a solution with respect to any form of silica is an important factor in determining whether that form will grow in an

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orderly manner into coarse aggregates or crystals, whether abundant nucleation will lead instead to many small crystals or crypto-crystals of that form, or whether an entirely different form will be deposited.

Because quartz (α modification) is the stable form of silica at temperatures below 573°C, all other forms deposited below this temperature are metastable and should change to quartz at varying rates depending on temperature, purity of the deposited material, presence or absence of water, and other factors.

Opal. Opaline sinter is formed at and near the vents of springs that are saturated with respect to amorphous silica. Not all precipitated silica, however, is actually deposited as opal. Direct evidence for deposition of opaline sinter at Steamboat Springs, for example, is surprisingly scanty. Much gelatinous silica settles in quiet pools and on the discharge aprons of springs, but most if not all of this silica eventually dries to a powdery dust when activity ceases at that spot, and is carried away by wind or water. Masses of gelatinous silica that have remained for a year or more in pools at 80° to 90°C show no obvious evidence of conversion to opal. Other samples have been stored in water at room temperature for as much as ten years without apparent formation of opal. Gelatinous masses of hot-spring algae, if desiccated as a result of shifting activity, also become light and powdery and are seldom preserved as sinter. If preserved under favourable circumstances, however, some masses harden after a few years. Repeated wetting and drying is probably essential to the hardening process. Dissolved silica precipitates when the water evaporates, and presumably cements the large polymeric molecules. The exact nature of the process is not yet known. These observations suggest that opal generally forms by direct precipitation of monomeric or, more probably, the smaller polymeric molecules of silica. Opal is probably not formed directly from large polymeric molecules, except where small molecules are also precipitated.

The type of sinter called geyserite provides some evidence for this hypothesis. Geyserite is characterized by an irregular, knobby, or colloform surface, and occurs near the vents of geysers and spouting springs. As compared to other types of sinter, it forms rapidly by evaporation of near-boiling water that is very high in silica. The silica of such waters, as previously shown, consists entirely or largely of the dissolved (monomeric) form. Evaporation and precipitation may be so rapid that the larger polymeric molecules do not have time to form.

Hard opal is also deposited below water-level in the vents of some springs that are supersaturated with respect to amorphous silica. Such opal has been observed in the Porcelain Terrace springs and the unnamed spring south-west of Pearl geyser of Norris Basin (see Table 2). No conspicuous opal is being deposited in normal spring vents at Steamboat, but active geyser vents contain some new opal. It seems probable that the sinter lining of many geyser vents is deposited during the steam phase following eruption, when water-level is low and films of water on rock surfaces are rapidly evaporated.

Opal has been found in veins and veinlets in drill core from a few sinter-depositing hot-spring areas (WHITE, 1955, p. 104). At Steamboat Springs, vein opal was found in drill core at depths as much as 75 ft, where temperatures are as high as 110°C. In places, opaline sinter has been found at greater depths, but is being

converted slowly to chalcedonic sinter. In Yellowstone Park, opal is also ordinarily restricted to shallow depths and to temperatures not much above boiling. A few veinlets were found by White (1955, p. 104) in Norris Basin drill core previously studied by Fenner (1936, pp. 282–310), from depths as much as 220 ft and temperatures close to 140°C. At the higher temperatures, opal is being converted to chalcedony. For amorphous opal to precipitate at 140°C, the concentration of dissolved silica must be at least 550 p.p.m., judging by extrapolation of Fig. 1 to this temperature. This suggests that the restriction of opal to lower-temperature environments may be due in part to the scarcity of waters saturated at high temperatures with respect to amorphous silica.

Opal of some hot-spring areas is also a characteristic end-product of near-surface leaching of silicate minerals by sulphuric acid. The acid is produced above the water table by oxidation of H_2S. The leached rocks are residually enriched in titania and silica, the latter remaining as opal. With sufficient time, even the opal is removed because of its appreciable solubility in acidified rain water or condensed steam. Because this acid type of alteration is related to the water table, replacement or residual opal is probably never formed at temperatures above 100°C.

The solubility of opal is assumed to be approximately the same as that of amorphous silica. This is suggested by Krauskopf's (1956) few experiments with opal and diatomite. Some opals are apparently amorphous, but X-ray studies have shown that some have a poorly developed structure, like that of cristobalite. It is likely that some differences in solubility, corresponding to differences in crystallinity, will be found.

Chalcedony. Chalcedony, a fibrous form of quartz, has not been recognized in primary hot-spring sinter or near-surface veins. Chalcedonic sinter, however, is abundant at Steamboat Springs in old sinters and those formed at depth, and has been recognized also at a few other hot-spring localities. All chalcedonic sinter was originally opaline; with sufficient time, temperature, and depth of burial, the opal was converted largely to chalcedony and in small part to quartz. The amount and type of impurities in the opal, and the rate of movement of water through the porous opaline mass may also be factors in determining the rate of conversion. The porosity of chalcedonic sinter is generally much less than that of opaline sinter in spite of the differences in densities of chalcedonic quartz and opal, because additional silica is deposited from the migrating water. The density of chalcedony is given in the literature (Berman, 1942) as 2·55 to 2·63 and that of opal as 1·9 to 2·3. The bulk density of opaline sinter at Steamboat Springs is generally of the order of 1·7. When opaline sinter is converted to chalcedonic sinter without change in volume, the bulk density is increased to about 2·5, by introduction of more silica.

The reconstitution of opal into chalcedony probably takes place through dissolution of opal and precipitation of the resultant monomeric silica as fibrous quartz. This reconstitution is for the most part a localized phenomenon, but migrating waters and diffusion may account for chalcedony that is depositing at some distance from the place where opal is being dissolved.

Compared to quartz, chalcedony shows a lower index of refraction (ω) and

density, and an appreciable content of water. Studies by HOFFMAN (1942) and by FOLK and WEAVER (1952) have clearly demonstrated that these differences are not ascribable to admixed opal but rather are due to the presence of large numbers of submicroscopic, water-filled vacuoles within the microcrystals of quartz. Factors that induce the fibrous habit of chalcedony are not known, but during crystallization much mother liquor becomes entrapped within the quartz fibres, probably because the degree of supersaturation and the rate of crystallization are somewhat higher than for macroscopic quartz.

Chalcedony may also form by sufficiently slow precipitation of small polymeric molecules of silica with simultaneous rearrangements to attain the quartz structure. Some irregular cavities in chalcedonic sinter are lined with bands of chalcedony that parallel the cavity walls on all sides except the bottom. Here, the layers are horizontal (except where disturbed by later deformation), and are thicker than elsewhere. The difference between bottom and sides must be due to influence by gravity. This points to the settling of colloidal particles of sufficient size. The particle size may be very small and the rate of settling may be exceedingly slow. There is no evidence to indicate whether these particles precipitated directly as chalcedony, or were first gelatinous silica that dissolved and crystallized as chalcedony.

Quartz. There is no evidence for direct precipitation of quartz in near-surface sinter or veins. The distributions of quartz and chalcedony are very similar at Steamboat Springs, except for the greater abundance of chalcedony. Both varieties of silica may result from reconstitution of opaline sinter, or from direct precipitation of silica in veins at depths of 50 ft or more. Fine-grained crystals with a mosaic habit grade from chalcedony to true quartz. Quartz of euhedral habit or with euhedral growth-lines is essentially restricted to cavities. Some cavities contain interbanded quartz and chalcedony as well as, rarely, opal. The last mineral to be deposited is nearly always quartz, and the last crystals are commonly the largest, ranging up to about 1 cm in length. Coarse crystals of quartz probably form from a solution that is only moderately supersaturated with respect to quartz at the temperature of deposition. Such a low-silica water is probably derived from the normal high-silica water by precipitation of chalcedony, after all available opal has been reconstituted.

Consider, for example, water that migrates from a major channel into horizontally-bedded sinter at a depth of about 75 ft and an initial temperature of about 130°C. If the water is supersaturated with amorphous silica, containing more than 375 p.p.m., a little opal can precipitate until equilibrium is attained. If the water, however, is unsaturated with respect to amorphous silica or if it is just saturated, chalcedony rather than opal will be precipitated. Any opal of buried sinter that is accessible to the water will go into solution, while chalcedony precipitates in open spaces. A part of the silica is derived directly from the water, which is still strongly supersaturated with respect to chalcedony. After all accessible opal has been reconstituted, and the permeability of the sinter has decreased greatly by deposition of chalcedony, the through-going water may become only moderately supersaturated with respect to quartz. Quartz will then be deposited rather than chalcedony.

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Temperature, rate of precipitation, and degree of supersaturation with respect to the different forms of silica are believed to determine which silica mineral is deposited. Quartz is generally favoured by moderately high temperature, but it possibly also forms below 100°C if the degree of supersaturation and the rate of precipitation are sufficiently low.

Cristobalite and tridymite. Some hot-spring opal, with indices of refraction as low as 1·46, has been called cristobalite because of its X-ray pattern. A small amount of definite cristobalite, with indices of refraction close to 1·485, has formed below the water table at Steamboat Springs at temperatures not much above 100°C. The relations of amorphous opal, of opal with an X-ray pattern of cristobalite, and of true cristobalite are not clear.

Tridymite in the Norris Basin drill core was ascribed by Fenner (1936, p. 305) to a hydrothermal origin. Fenner's drill core has been restudied by White (1955, pp. 108–110) who found the tridymite and associated sanidine to be pneumatolytic and related to extrusion of the rocks as welded tuffs.

At Mount Lassen, California, Anderson (1935, pp. 242–248) found tridymite forming in lavas that were being altered by sulphuric acid at temperatures close to 90°C, and Daubrée (1876) described the alteration of Roman bricks to zeolites, opal, and tridymite at temperatures as low as 73°C at Plombières, France.

The origin of cristobalite and tridymite in hot springs is not clear. The minerals have formed metastably, at temperatures far below equilibrium temperatures, and in contact with waters that were strongly supersaturated in silica with respect to the stable mineral quartz.

Origin of the Clay Minerals

Hydrothermal clay minerals. Clay minerals are usually assumed to form by selective leaching, for example, of calcium from calcic feldspar, followed by reconstitution of the remaining silica and alumina in some unspecified manner. Although the origin of clay minerals is not within the main scope of this paper, the properties of silica suggest a possible explanation. It seems likely that monomeric alumina as well as monomeric silica are the fundamental "building blocks." In the past, alumina as well as silica has usually been considered colloidal, but some alumina may be monomeric. In view of the fact that total alumina is seldom more than 1 p.p.m. in most near-neutral waters, the concentration of "dissolved" alumina must necessarily be very low. The slow rate of dissolution of silica and perhaps alumina at low temperature, and the very low solubility of alumina at pH 5 to 9, the range in which most clays are formed, can account for the failure to synthesize clearly-identifiable clay minerals at low temperature (Grim, 1953, pp. 321–322).

The moderately high temperatures of many hot springs probably favour relatively high rates of reaction in the formation of hydrothermal clay minerals.

Clay and bauxite minerals of soils. The geochemistry of silica is applicable to other geologic problems. If hydrothermal clays are formed in the manner just proposed, a similar origin is indicated for clays formed by weathering.

The origin of bauxite may be a similar problem. Ordinary rocks and soils contain much silica, so that 10 to 50 p.p.m. of soluble silica is ordinarily—though

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perhaps slowly—dissolved in rain water that percolates into the ground. The high silica content, relative to alumina, is probably sufficient under usual conditions to keep the proposed reaction, dissolved silica + dissolved alumina $\rightleftharpoons$ clay, displaced strongly to the right. With sufficient time, all susceptible minerals are weathered to clays, and excess free silica is removed from the soil zone. Under conditions of tropical rainfall and temperature, the proposed reaction could then be displaced significantly to the left by dissolution and removal of silica from the residual alumina in an open system. Alumina, because of its much lower solubility in near-neutral solution, remains as bauxite.

CONCLUSIONS

Our conclusions, wherever on common ground, are in almost complete agreement with those of KRAUSKOPF (1956) that were based on laboratory experimentation.

1. Nearly all silica of hot springs is in true molecular solution, probably as H_4SiO_4. Solubility of amorphous silica at Steamboat Springs, as determined by the colorimetric molybdate method, is about 315 p.p.m. of SiO_2 at 90°C, and aged samples of neutral and alkaline waters attain equilibrium at about 110 p.p.m. at 25°C. If the colour intensity is decreased somewhat by salinity, as has been shown for sea water, the actual solubility curve for hot springs is somewhat higher and is very close to KRAUSKOPF's curve. Solubility is at least as high in acid as in alkaline springs, but equilibrium is attained, in acid solutions, at exceedingly slow rates.

2. In supersaturated solutions at low temperature, monomeric silica polymerizes slowly to colloidal silica. The rate may be almost infinitely slow in acid water and in solutions that are only moderately supersaturated. The rate of polymerization is increased by high pH, high temperature, high degree of supersaturation, the presence of previously formed colloidal silica, and contact with some other substances. Opaline sinter is particularly effective, but chalcedonic sinter appears to have the opposite effect. Algae are, at best, only a minor factor.

3. Precipitation of colloidal silica is favoured by high temperature and, to some degree, by all substances that were tested, notably opaline sinter, but chalcedonic sinter is also influential.

4. Many connate and other ground waters, including nonvolcanic thermal springs and volcanic springs of the calcium-bicarbonate type, are notably unsaturated with respect to amorphous silica. Precipitation of quartz and chalcedony, the common low-solubility forms of silica, is believed to be the principal explanation.

5. Opal and gelatinous silica are formed when silica is deposited with relative rapidity. Opal is favoured by low temperature. It occurs at temperatures as high as 140°C, but it is unstable and is converted slowly to chalcedony or quartz. Opal is probably formed from monomeric or, more probably, the smaller polymeric molecules of silica. Evidence is lacking for the direct conversion of gelatinous silica to opal at room temperature.

6. Formation of quartz is believed to be favoured by relatively high temperature, slow rate of deposition, and low degree of supersaturation, and is probably formed directly from monomeric molecules.

7. Chalcedony is probably formed from waters that are rather strongly super-saturated with respect to quartz. The rate of deposition may be too rapid for attainment of the well-ordered structure of quartz.

8. Clay minerals may form from monomeric silica and monomeric alumina as the fundamental "building blocks." Dissolved alumina, if it exists, does not exceed 1 p.p.m. in near-neutral solution at low temperature. Slow rates of dis-solution of soluble alumina, comparable to those of silica, could account for failures to synthesize clay minerals at low temperatures. Because of the abundance and relatively high solubility of silica, the proposed reaction, dissolved silica + dissolved alumina $\rightleftharpoons$ clay, is ordinarily displaced strongly to the right. With dissolution and removal of silica in an open system, aided by tropical rainfall and temperature, the reaction may be displaced to the left. Alumina, because of its very low solubility, remains as bauxite.

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