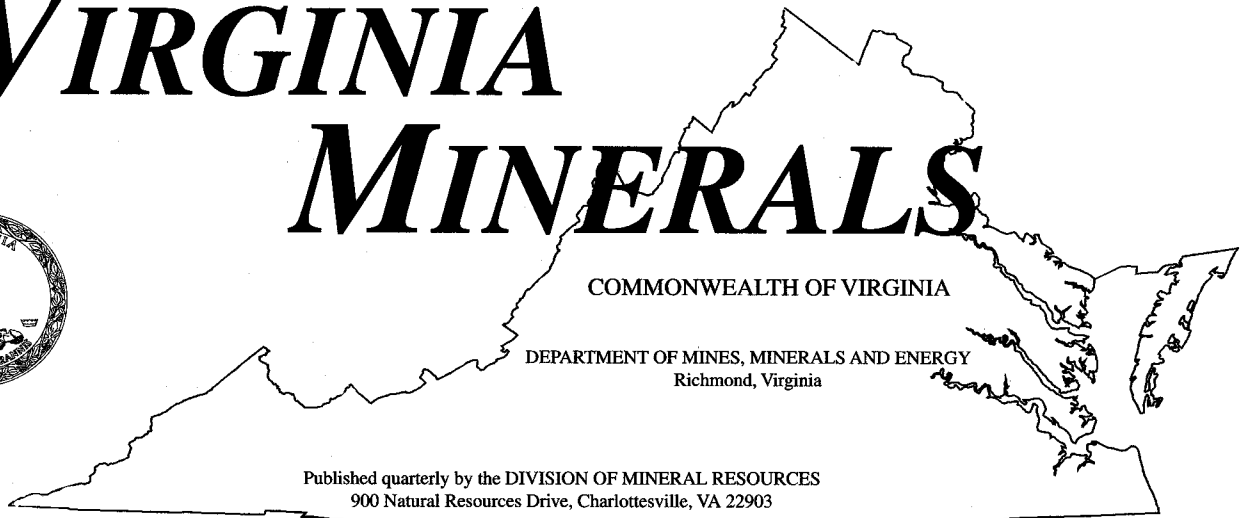


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ANCIENT WARM SPRINGS DEPOSITS IN BATH AND ROCKINGHAM COUNTIES, VIRGINIA

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INTRODUCTION

Springs are of interest and importance to man not only because of their beauty and recreational potential, but also because of their water supply and medicinal value. Thermal or warm springs are present in the Valley and Ridge province of Virginia in the western counties along the West Virginia boundary (Figure 1). Reeves (1932) presented a comprehensive study of the occurrence, chemical, and physical characteristics of warm springs. The present study addresses deposits associated with two geologic and topographic features in Bath and Rockingham Counties. It will be argued in this paper that these are ancient warm spring conduits or outflow features similar to deposits described from Nevada, California, and Queensland, Australia. As gold is produced from many such deposits, the Virginia sites may have potential for precious metal mineralization.

CHARACTERISTICS OF VIRGINIA'S WARM SPRINGS

Natural springs are sites at which groundwater flows to the surface and issues freely from the ground. Groundwater is insulated from fluctuations in air temperature and therefore approaches the mean annual air temperature for the area. A spring whose flow is at least 9°F (5°C) higher than this mean temperature and lower than 100°F (38°C) is classified as a warm spring. A spring whose flow is warmer than 100°F is classified as a hot spring. The mean annual air temperature in northwestern Virginia ranges between 48° and 54°F. Reeves (1932) has shown that, in this area, water temperatures in springs range from 55° to 106°F. From a sample of 85 springs,

72 temperatures fall between 55° and 75°F.

Two models have been proposed for the temperature of warm springs. These are: shallow circulation above a still-cooling pluton and deep circulation of groundwater which is structurally controlled. Heat flow studies (Costain and others, 1976) have shown no evidence for the existence of a shallow pluton. Costain and others (1976) and Perry and others (1979) reported that the geothermal gradient in the area to be about 1.5°F/100 ft (10°C/km). They concluded that the warm springs in Virginia are not associated with a cooling pluton. Instead they attribute the warm springs to deep circulating groundwater. Assuming a constant gradient remains at depth, water would have to circulate to a depth of about 26,000 feet to be heated to the temperature observed at the surface. Since basement lies about 32,500 feet below the surface (Harris, 1975), deep circulation in the sedimentary section is possible.

In this report, we restricted the term "sinter" to deposits consisting dominantly of silica minerals formed at the surface by deposition from thermal waters. Spring deposits consisting dominantly of carbonate minerals are called travertine. The spring deposits discussed in this paper are sinters.

LOCATION AND GEOLOGIC SETTING

Two possible warm springs' deposits were discovered during the field investigations for carbonate rock resources. The first site near Broadway (Figure 2) in Rockingham County was discovered in December, 1983; the second site near Warm Springs (Figure 3) in Bath County was discovered in August, 1988.

Bedrock in the Broadway area consists of the Cambrian-

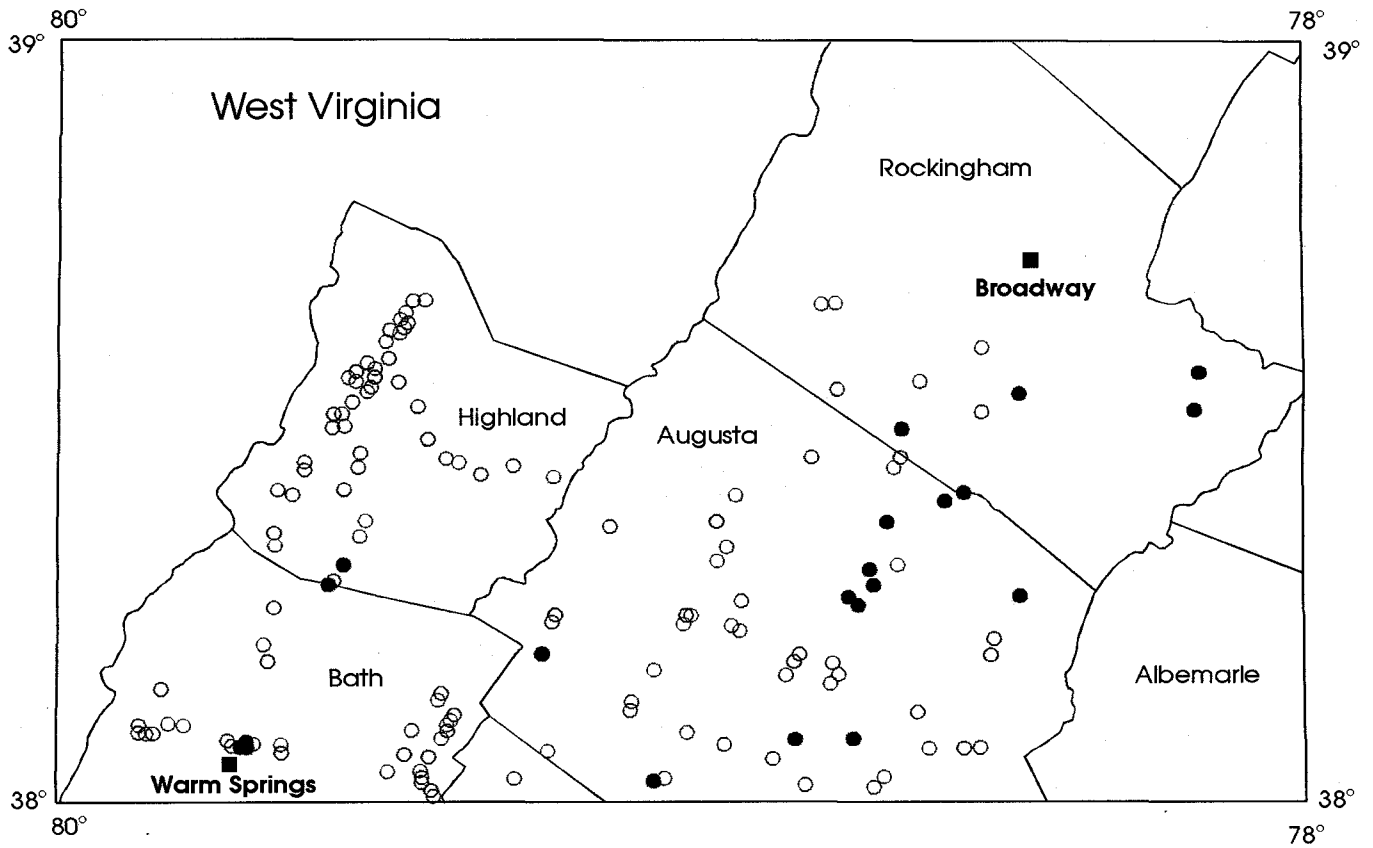


Figure 1. Location of the Broadway and Warm Springs sites in relation to the occurrence of warm springs (solid dots) and cold springs (open circles).

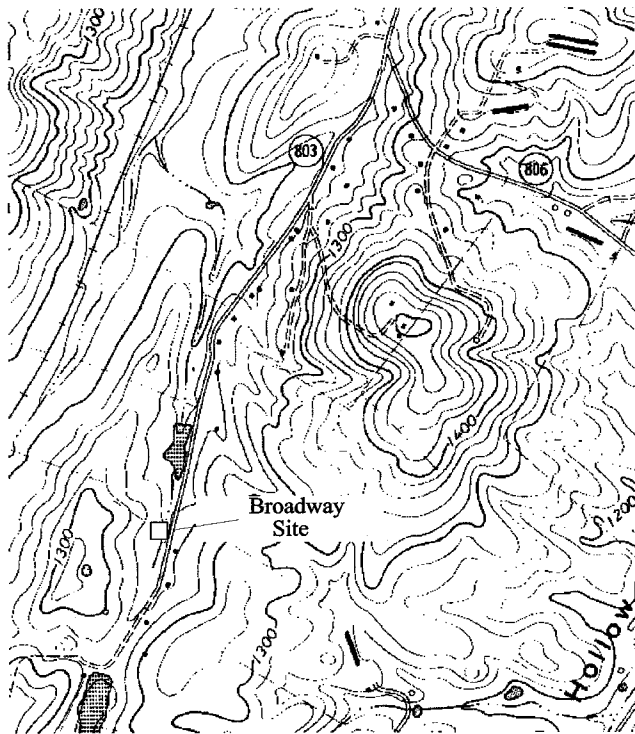


Figure 2. Location of the Broadway site, Broadway 7.5-minute topographic map.

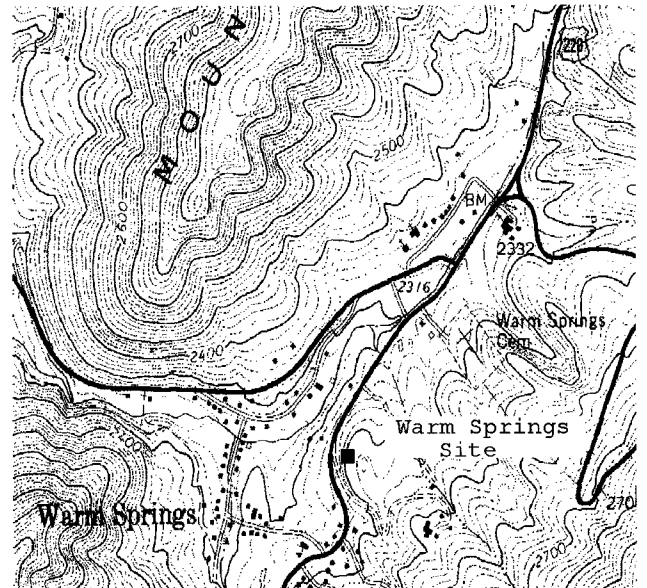


Figure 3. Location of the Warm Springs site, Warm Springs 7.5-minute topographic map.

Ordovician-age Conococheague Limestone and the Ordovician-age Stonehenge Limestone, Beekmantown Formation, New Market and Lincolnshire Limestones, and Edinburg and Martinsburg Formations. The New Market Limestone is composed of thick bedded, medium to dark gray, fine grained limestone. The rock breaks with a conchoidal fracture and emits a ringing sound when struck with a hammer. The New Market weathers to a light gray and weathered surfaces are typically rounded and fluted. It contains an abundance of gastropods as shown by etched outlines of the whorls on weathered surfaces. The Broadway site (Figure 2) is located on the west side of State Road 803 about 10.8 miles south of the Town of Broadway. At this site, banded siliceous sinter crops out between exposures of Beekmantown Formation and New Market Limestone, on the southeast limb of a syncline. The section between the banded siliceous sinter outcrop and the Beekmantown Formation is not exposed. The topographic feature formed by the siliceous sinter is a low-oval-shaped hill, 10 to 12 feet high, and about 200 feet long, with the widest section approximately 75 feet. Siliceous sinter-float is present on the northeast and north slopes of the hill (Figure 2). Banded siliceous sinter outcrop occurs near the top of the hill along the northwest-side. Individual beds generally range from 6 inches to 2 feet in thickness. Relict stratification is observable in individual beds, although the sinter generally does not break readily along stratification planes in beds. Fresh surfaces range in color from white to light gray and are streaked or mottled pink or red. Some highly colored sinters are dark gray upon weathering.

Bedrock units in the Warm Springs area are similar to those in the Broadway area (Figure 4) and the Ordovician Juniata Formation and the Silurian Tuscarora Sandstone, Rose Hill Formation, and Keefer Sandstone are also present. The second site occurs in Bath County near the Town of Warm Springs (Figures 1 and 3). The Edinburg Formation, near Warm

Springs, is composed of thin to medium bedded, dark gray, fine grained limestone. Some beds contain abundant fossil fragments, typically trilobites, crinoids, brachiopods, and bryozoans. An excellent exposure is visible along the southeast bank of State Highway 220 at the Warm Springs site. At this site, along the axis of the Warm Springs anticline, the entire feature is a siliceous sinter that replaced a portion of the Edinburg Formation. Pyrite, sulfates, and black, carbon-rich sinter occur near the base of the outcrop. Brecciation and open cavities are present in many zones along the 200-foot exposure and along the 10-foot high bank. The Edinburg Formation crops out on the southwestern end of the deposit. The strike and dip of this limestone are not compatible with that of the carbonate-rocks in the nearby area. Eruptive or explosive activity of solutions in the area may have contributed to the disruption of the limestone near the conduit.

Hydrothermally altered New Market Limestone and Edinburg Formation is composed dominantly of chalcedonic sinter. The sinter contains little or no opal. Fine-grained quartz in cavities is commonly detectable with the hand lens. Sinter has a dull luster similar to unglazed porcelain. The sinter weathers white to light gray on fresh surfaces with some iron-staining. Masses and crusts of limonite are associated with the sinter.

METHOD OF ANALYSIS

A total of 40 samples, 30 of altered (siliceous sinter) rock and 10 unaltered rock, were collected from the ancient warm spring deposits in Bath and Rockingham Counties. Sixteen composite samples over a twenty-foot interval of altered Edinburg Formation (siliceous sinter) were collected from the Warm Springs site (Figure 5). Additionally three samples of unaltered Edinburg Formation were collected for background information. Fourteen composite samples of altered New Market Limestone were collected from the

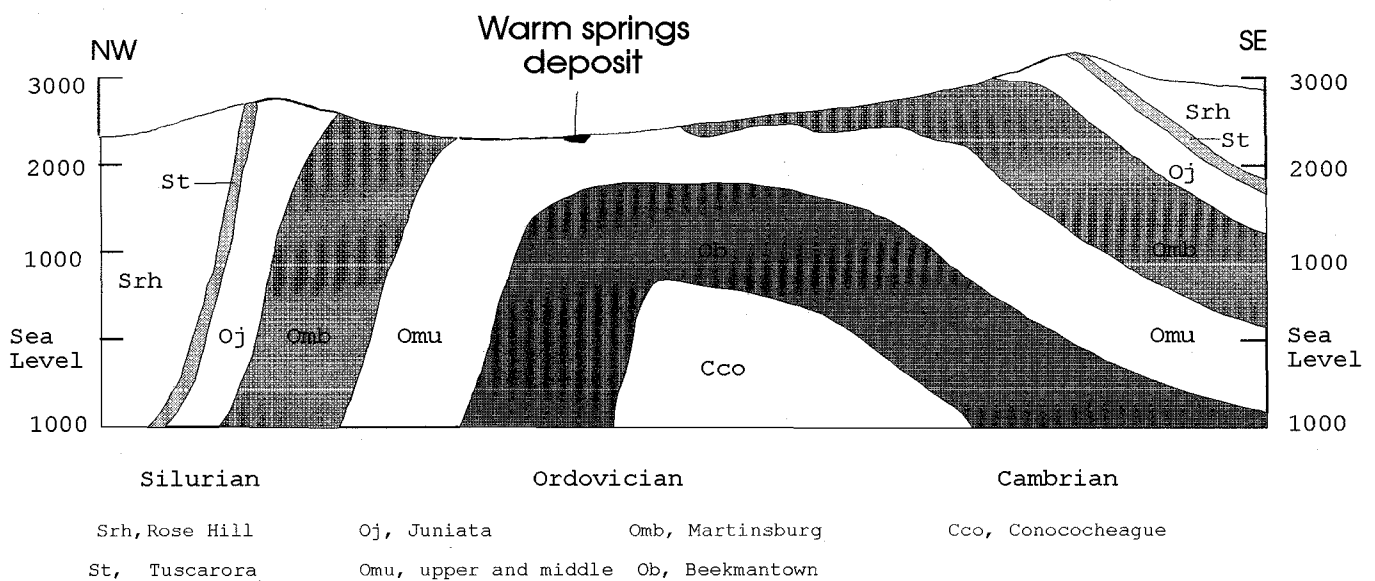


Figure 4. Structural cross section through the Warm Springs site.

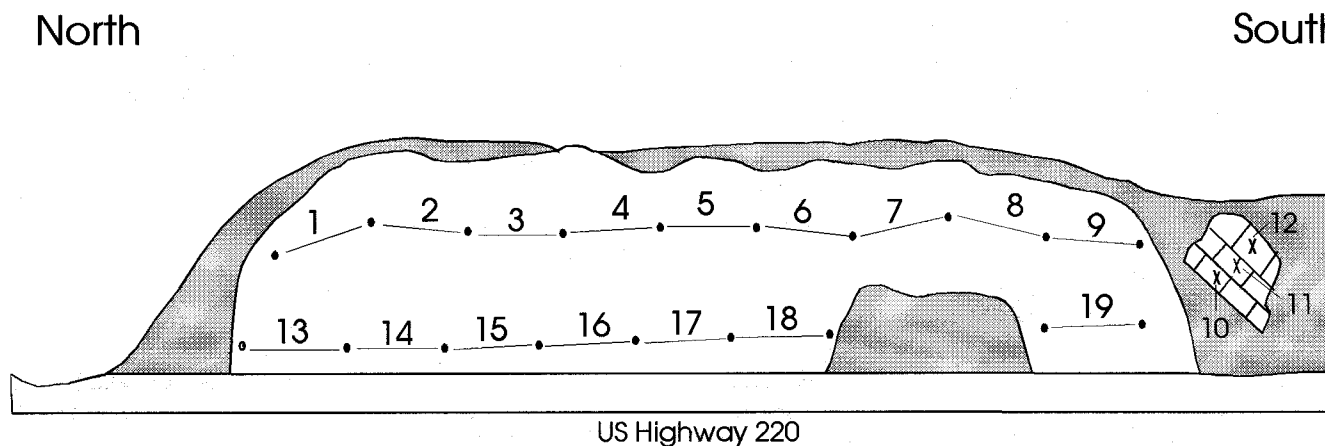


Figure 5. Vertical section through the Warm Springs site showing approximate locations of samples. Stippled areas are covered intervals.

Broadway site. Also seven samples of unaltered New Market Limestone were collected to provide background information (Giannini, 1994; Giannini and Hostettler, 1994). The composite samples consisted of chips to 3-inches across. Six samples of unaltered rock and six samples of altered rock were studied under the petrographic microscope. X-ray diffraction analysis was performed on one sample of New Market Limestone and Edinburg Formation. Two samples for altered rock from Warm Springs and three samples from the Broadway site were X-rayed.

Major, minor, and trace element analyses were determined for all forty samples. The oxides of Si, Al, Ca, Na, K, Fe, Mn, Ti, and P and loss on ignition (LOI) were done by X-ray fluorescence with a detection limit of 0.01 percent. Trace elements analyzed for and their detection limits are as follows: Ag(0.5), As(1.0), Au(1.0), B(10.0), Ba(10.0), Bi(3.0), Cd(1.0), Co(1.0), Cu(0.5), Ga(3.0), Ge(10.0), Mo(1.0), Ni(1.0), Pb(2.0), Rb(10.0), Sb(0.2), Sr(10.0), and Zn(0.5). All elemental values are in parts per million (ppm) except gold that is in parts per billion (ppb). Ag, Cd, Co, Cu, Mo, Ni, Pb, and Zn were determined by inductively coupled plasma-atomic emission spectrometry (ICP). As and Sb were analyzed by instrumental neutron activation analysis (INAA); Au, B, Bi, and Ge were done by direct current plasma-atomic emission spectrometry (DCP).

The trace element concentration data show a logarithmic distribution, when plotted as a frequency histogram. Therefore, the interpretation of trace element data was done based on log transformation data. Trace element means and threshold (mean plus two standard deviations), based on the logarithmic data, was converted back to ppm for reader convenience. All values above the threshold are considered anomalous (may show mineralization); however, lower values may be anomalous.

MINERALOGY AND GEOCHEMISTRY OF SURROUNDING ROCKS AND SINTER

Thin section and X-ray diffraction analyses of the un-

tered New Market Limestone and Edinburg Formation shows calcite to be the dominant mineral. Also present in these rocks is quartz and illite.

In thin section, the sinters are composed of microcrystalline and chalcedonic quartz. The microcrystalline quartz is composed of interlocking grains in random orientation. The individual grains in samples average three to five microns in diameter. The aggregate has "pinpoint" birefringence, but in some samples the grains are so small they appear isotropic. Each grain appears to possess undulous extinction. Chalcedonic quartz is composed of radiating bundles of fibers, each fiber not more than a few microns in diameter and ranging up to 150 microns or more in length. The boundary between the chalcedonic and microcrystalline quartz may be sharp, with some transitional areas. X-ray diffraction analyses of the sinters show the presence of quartz, illite, limonite, and fluorite.

Seven samples of New Market Limestone and three samples of Edinburg Formation were chemically analyzed for comparison of unaltered and altered (sinter) rock. The mean values for the major, minor oxides, LOI, and trace elements for unaltered samples are presented in Table 1. For unaltered samples calcium oxide (CaO) in the New Market Limestone is 54.4 percent and in the Edinburg Limestone is 47.9 percent. The silica content for these units average 1.4 percent and 9.5 percent, respectively. Aluminum oxide content is 0.18 percent in the New Market and 2.8 percent in the Edinburg. The remaining oxides accounted for less than 1.8 percent for both units. Table 1 presents the data for trace elements.

Chemical analyses of 14 samples of altered New Market Limestone from Broadway (Table 2) shows that SiO₂ is the dominant oxide, 92.4 percent, followed by Al₂O₃, 1.9 percent and CaO makes up only 1.4 percent. The 16 samples of altered Edinburg Formation from Warm Springs area contains 84.9 percent, followed by Al₂O₃, 2.4 percent and CaO makes up only 4.9 percent. The most prominent feature of the altered rock samples is an enrichment of silicon, iron, and aluminum, and a loss of calcium and magnesium, with a less marked gain

Table 1. Composition of unaltered New Market Limestone and Edinburg Formation samples.

Variable	Broadway New Market limestone	Warm Springs Edinburg limestone
Samples	7	3
Major and minor oxides (percent)		
SiO ₂	1.44	10.28
Al ₂ O ₃	0.18	2.83
CaO	54.42	47.8
MgO	0.64	0.5
Na ₂ O	0.08	0.02
K ₂ O	0.04	0.53
Fe ₂ O ₃	0.19	0.7
MnO	0.01	0.02
TiO ₂	0.01	0.09
P ₂ O ₅	0.05	0.05
S	0.01	0.03
LOI	<u>42.73</u>	<u>36.73</u>
Total	99.8	99.58
Trace Elements (parts per million)		
Antimony	<0.2	0.2
Arsenic	1.1	1
Barium	<10	<10
Bismuth	<3	3.5
Boron	<10	55.9
Cadmium	<1	<1
Cobalt	<1	1.8
Copper	<0.5	7.5
Gallium	6.5	15.3
Germanium	10	22.9
Gold (ppb)	<1	<1
Lead	<2	4.6
Lithium	<10	<10
Molybdenum	<1	<1
Nickel	1	6.2
Rubidium	<10	<10
Silver	<0.5	1.2
Strontium	271.5	558.1
Zinc	7.06	29.1

in titanium. The Broadway sinters data also show barium, gallium, lithium, and strontium to have contents greater than the threshold in about half of the samples (Table 3). Several samples have elevated arsenic, boron, rubidium, and zinc. For the Warm Springs sinter barium, gallium, rubidium, and strontium are elevated. Several samples have elevated arsenic, bismuth, boron, copper, lead, and zinc.

Only three samples of siliceous sinter (Figure 5; Table 4) from the Warm Springs site contained gold contents greater than or equal to the detection limit for gold. Samples 1 and 6 contained 2 parts per billion (ppb) gold and sample 18 contained only 1 ppb. The three samples of unaltered

Table 2. Composition of altered New Market limestone and Edinburg limestone.

Variable	Broadway New Market limestone	Warm Springs Edinburg limestone
Samples	14	16
Major and minor oxides (percent)		
SiO ₂	92.48	84.91
Al ₂ O ₃	1.96	2.45
CaO	1.41	4.92
MgO	0.22	0.21
Na ₂ O	0.03	0.01
K ₂ O	0.31	0.64
Fe ₂ O ₃	0.93	3.24
MnO	0.07	0.01
TiO ₂	0.09	0.22
P ₂ O ₅	0.06	0.04
S	0.03	0.57
LOI	<u>1.65</u>	<u>2.16</u>
Total	99.24	99.38

Edinburg Formation (samples 10, 11, and 12) have less than the detection limit for gold (1 ppb). All the samples of siliceous sinter except one (sample 8) and the seven unaltered New Market Limestone samples from the Broadway site contained a gold content less than the detection limit. Sample eight contained 3 ppb gold.

Samples 1 through 6 (Figure 5) from the Warm Springs site contained silver less than the detection limit for silver (0.5 parts per million, ppm). Samples 7, 8, 9, and 13 through 19 contained silver contents ranging from 0.8 to 1.4 ppm. The three samples of unaltered Edinburg Formation contained 1.2, 1.4, and 1.1 ppm silver. All of the samples from the Broadway site contained silver of less than the detection limit. An additional analysis of the siliceous sinter-breccia from the Broadway site showed 2 ppm (0.06 ounces per ton) of silver.

SILICA GEOCHEMISTRY

Silica solubility increases with increase in temperature (Figure 6) (White and others, 1992). Silica will dissolve until the solution is saturated often faster than it precipitates from an oversaturated solution. Thus, thermal water will dissolve silica minerals as its temperature rises, but as the water cools silica will be precipitated. The actual silica concentration in water depends on the particular silica mineral exposed to the water, and to the temperature and the rate of the dissolution. Figure 6 shows solubilities of chalcedony and quartz. The change of opal into chalcedony (White and others, 1956) probably takes place through a dissolution of opal. Then the resultant monomeric silica is precipitated as fibrous quartz. The change is, for the most part, a local phe-

Table 3. Trace element content of altered New Market and Edinburg limestones (ppm=parts per million; L=less than detection limits).

Trace Elements	Detection Limits (ppm)	Broadway Siliceous Sinter N=14			Warm Springs Siliceous Sinter N=16		
		Mean (ppm)	Threshold (ppm)	Number of Samples above Threshold	Mean (ppm)	Threshold (ppm)	Number of Samples above Threshold
Antimony	0.2	0.3	0.5	2	0.3	0.4	2
Arsenic	1.0	19.7	22.5	3	15.7	18.0	6
Barium	10.0	87.9	99.1	8	1105.3	111.5	8
Bismuth	3.0	L			4.4	6.7	3
Boron	10.0	20.8	23.3	5	39.5	42.7	4
Cadmium	1.0	L			L		
Cobalt	1.0	3.8	7.4	2	L		
Copper	0.5	5.9	7.7	2	7.1	9.5	5
Gallium	3.0	15.2	17.0	8	16.9	18.2	8
Germanium	10.0	L			L		
Gold (ppb)	1.0	L			1.1	2.7	0
Lead	2.0	3.9	6.2	2	8.8	10.6	4
Lithium	10.0	104.9	106.4	9	49.9	51.0	1
Molybdenum	1.0	L			1.1	2.7	0
Nickel	1.0	4.3	6.4	1	8.8	10.6	4
Rubidium	10.0	17.9	20.6	4	24.1	26.8	10
Silver	0.5	L			0.9	1.5	0
Strontium	10.0	13.9	16.1	6	51.7	54.9	9
Zinc	0.5	56.2	67.2	5	8.8	13.8	4

Table 4. Gold and silver concentrations for siliceous sinter samples from the Warm Springs site.

Sample Number	Silver (ppm)	Gold (ppb)
1	<0.5	2.0
2	<0.5	<1.0
3	<0.5	<1.0
4	<0.5	<1.0
5	<0.5	<1.0
6	<0.5	2.0
7	1.4	<1.0
8	1.2	<1.0
9	1.3	<1.0
13	0.9	<1.0
14	1.0	<1.0
15	1.0	<1.0
16	0.9	<1.0
17	0.8	<1.0
18	1.2	1.0
19	1.0	<1.0

nomenon. Migrating waters and diffusion may account for chalcedony that is depositing at some distance from the place where waters are dissolving the opal.

Chalcedony is also formed by slow precipitation of small polymeric molecules of silica with simultaneous rearrangement to attain the quartz structure. In the occurrences studied, bands of chalcedony line some irregular cavities in chalcedonic sinter that parallel the cavity walls.

The distribution of quartz and chalcedony are very similar. Both varieties of silica may result from reconstitution of opaline sinter. They may also form by direct precipitation of silica in veins at depths of 50 feet or more. Fine-grained crystals with a mosaic habit grade from chalcedony to true quartz. When water is unsaturated with respect to amorphous silica or if it is just saturated, chalcedony rather than opal is precipitated.

ORIGIN OF SILICEOUS SINTER

Rimstidt and Cole (1983) recognized three steps in the formation of siliceous sinter. First, a geothermal solution that is in equilibrium with quartz in the surrounding rock flows to the surface and becomes supersaturated with amorphous silica as it cools. Then amorphous silica particles combine to make a colloidal suspension. Finally, the suspended amorphous silica particles agglomerate to form sinter.

The formation of siliceous sinter requires that the geothermal fluids contain a high silica concentration and become satu-

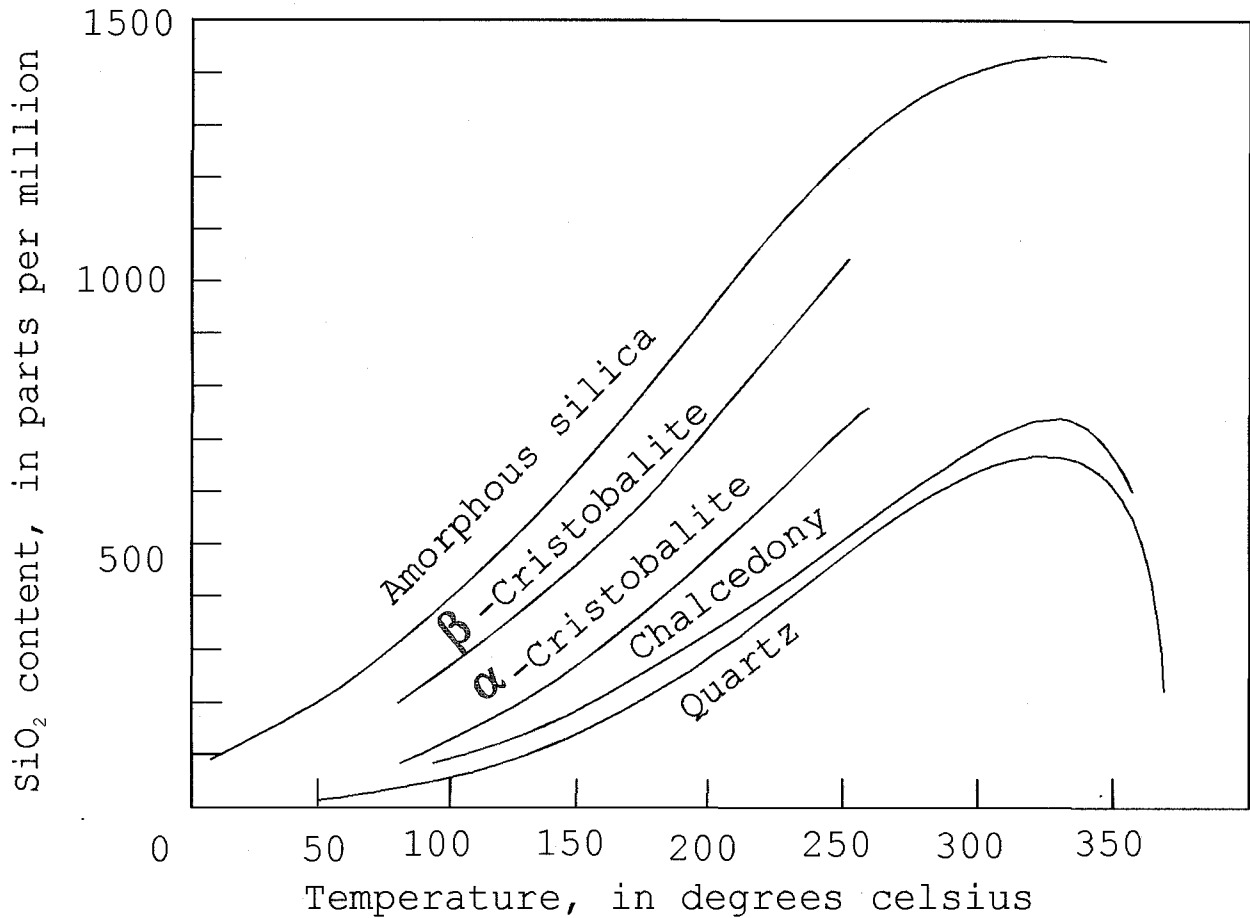


Figure 6. Solubilities of silica minerals in water as a function of temperature (modified from White and others, 1992).

rated with amorphous silica when they cool through the range of 100° to 50°C range. The solubility of quartz generally controls the silica concentration of the fluid under reservoir conditions (Fournier and Rowe, 1966). As an example, when a spring is depositing amorphous silica sinter at 100°C, the water must contain at least 370 ppm dissolved silica. A reservoir hotter than 235°C is required to produce this concentration (Figure 6), provided there is no boiling (Rimstidt and Barnes, 1980). The thermal spring that deposited these sinters appear to consist entirely of meteoric water that has circulated to considerable depth where the geothermal gradient is "normal." Silica in this water is derived from alteration and solution of rocks through which the water migrated. Chalcedonic sinter was originally opaline; with sufficient time, temperature, and depth of burial, the opal converted to chalcedony and microcrystalline quartz.

In the Warm Springs area system (Figure 4), the potential sources of silica are the Silurian Tuscarora Sandstone and the Ordovician Martinsburg Shale. Other sources of silica could be the bentonites associated with the lower part of the Trenton (lower Martinsburg) and the underlying Eggleston Formation. Rain water percolating through these formations along the northwestern steep limb of the Warm Springs anticline was heated by a normal geothermal gradient. As the waters flowed downward through the sandstones

and shales, silica was dissolved with the increasing temperature and pressure. Also the trace elements, barium, gallium, rubidium, and strontium were dissolved from the clay minerals in the shales. Then the water rose rapidly along an essentially vertical east-west fracture zone that intersect the bedding plane permeability at depth in the Late Ordovician limestones throughout the area. As the water flowed toward the crest of the Warm Springs anticline, it would mix with alkaline meteoric waters from the near surface and cool down. The resulting cooler water would cause the amorphous silica and aluminum particles to combine to make a colloidal suspension. The presence of ferric hydroxides helped this combination. As the suspension of silica and aluminum colloidal particles cooled some of the silica and aluminum along with the trace elements combined to form clays, especially illite. As the suspension cooled further, the suspension became oversaturated with amorphous silica particles, collecting into a pile and were cemented to form sinter along the surface of the ground when it flowed.

SUMMARY

Two ancient warm spring deposits comprised of siliceous sinter occur in Bath and Rockingham Counties. The Bath County site near Warm Springs is hydrothermally altered

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Edinburg Formation. The Rockingham site is hydrothermally altered New Market Limestone. Both sites are enriched in barium, gallium, lithium, and strontium through processes of dissolution of these trace elements as waters percolated through the shales and sandstones. There appears to be no anomalous concentrations of gold or silver, although one sample from the Broadway site indicates 2 ppm (0.06 ounces per ton) silver. Also at the Warm Springs site, copper, lead, and zinc are in anomalous concentrations.

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