Journal of Volcanology and Geothermal Research 310 (2016) 132–136

Contents lists available at ScienceDirect

Journal of Volcanology and Geothermal Research

journal homepage: www.elsevier.com/locate/jvolgeores

Short communication

Radiocarbon dating of silica sinter deposits in shallow drill cores from the Upper Geyser Basin, Yellowstone National Park

Jacob B. Lowenstern [a,*], Shaul Hurwitz [a], John P. McGeehin [b]

[a] U.S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94025, USA
[b] U.S. Geological Survey, 12201 Sunrise Valley Drive, MS-926A, Reston, VA 20192, USA

ARTICLE INFO

Article history:
Received 9 October 2015
Accepted 10 December 2015
Available online 19 December 2015

ABSTRACT

To explore the timing of hydrothermal activity at the Upper Geyser Basin (UGB) in Yellowstone National Park, we obtained seven new accelerator mass spectrometry (AMS) radiocarbon ^{14}C ages of carbonaceous material trapped within siliceous sinter. Five samples came from depths of 15–152 cm within the Y-1 well, and two samples were from well Y-7 (depths of 24 cm and 122 cm). These two wells, at Black Sand and Biscuit Basins, respectively, were drilled in 1967 as part of a scientific drilling program by the U.S. Geological Survey (White et al., 1975). Even with samples as small as 15 g, we obtained sufficient carbonaceous material (a mixture of thermophilic mats, pollen, and charcoal) for the ^{14}C analyses. Apparent time of deposition ranged from 3775 ± 25 and 2910 ± 30 ^{14}C years BP at the top of the cores to about 8000 years BP at the bottom. The dates are consistent with variable rates of sinter formation at individual sites within the UGB over the Holocene. On a basin-wide scale, though, these and other existing ^{14}C dates hint that hydrothermal activity at the UGB may have been continuous throughout the Holocene.

Published by Elsevier B.V.

1. Introduction

Yellowstone's hydrothermal system consists of more than 10,000 diverse thermal features, including geysers and non-erupting springs and pools that deposit siliceous sinter from neutral, Cl-bearing thermal waters (Fournier, 1989; Hurwitz and Lowenstern, 2014). A significant proportion of Yellowstone's silica-saturated waters issue from thermal springs in the Firehole River drainage, including from the iconic geysers of the Upper Geyser Basin (UGB) (Fig. 1). Approximately 33% of Yellowstone's chloride flux comes from the Firehole River (Hurwitz et al., 2007), and about one-third of that derives from the UGB (Allen and Day, 1935; Fournier et al., 1976). Intact sinter deposits of the UGB (~2.5 km^2) presumably formed after the end of the Pinedale glaciation, which was at its maximum on the Yellowstone Plateau 14.6 ± 0.7 kyr ago (^{10}Be exposure ages of moraines in Licciardi and Pierce, 2008). Older deposits include Pinedale-aged and older hydrothermally cemented glacial till deposits (kame) and outcrops of late Pleistocene rhyolite flows (Muffler et al., 1982).

Thermal waters currently discharging in the UGB have elevated concentrations of chloride, sodium, and silica (Hurwitz et al., 2012). As thermal waters cool following discharge, the solubility of silica (SiO_2) decreases (Fournier, 1985), leading to precipitation of opal-A and deposition of siliceous sinter that forms cones, domal mounds, and terraces. Repeated wetting and evaporation of surfaces and capillary effects are the main controls on the deposition, morphology, and microstructure of the sinter. Particles of rock, plant matter, charcoal, pollen, and other materials can be trapped in the sinter as it grows. The abundance of microbial filaments within the sinter deposits also suggests that some biotic processes are involved (Lowe and Braunstein, 2003; Guidry and Chafetz, 2003; Jones et al., 2001; Campbell et al., 2015).

The timing of post-glacial hydrothermal activity in Yellowstone's geyser basins is poorly constrained because only a few published radiometric dates of associated deposits are available. Wood embedded in Old Faithful geyser's sinter mound that was radiocarbon dated by Marler (1956) yielded a ^{14}C age of 730 ± 200 years BP (years before present; 0 years BP = 1950 A.D.). Radiocarbon dating of organic matter trapped in sinter has been successfully used at a number of geothermal areas (Foley, 2006; Lynne et al., 2005, 2008; Howald et al., 2014). Using similar techniques, Castle Geyser's shield (Fig. 1) yielded ages of 10,472 ± 70 and 8787 ± 60 years BP and three dates from the geyser's cone range between 1038 ± 35 and 926 ± 35 years BP (Foley, 2006). Uranium-series disequilibrium dating of two samples from a siliceous spire in northern Yellowstone Lake yields ages of ~11,000 years (Morgan et al., 2007). In this study, our primary goal was to determine whether there is evidence that hydrothermal activity (and sinter deposition) in the Upper Geyser Basin continued during the period in between the two sets of dates found at Castle Geyser (cf. Fournier,

* Corresponding author.
E-mail address: jlwnstrn@usgs.gov (J.B. Lowenstern).

http://dx.doi.org/10.1016/j.jvolgeores.2015.12.005
0377-0273/Published by Elsevier B.V.

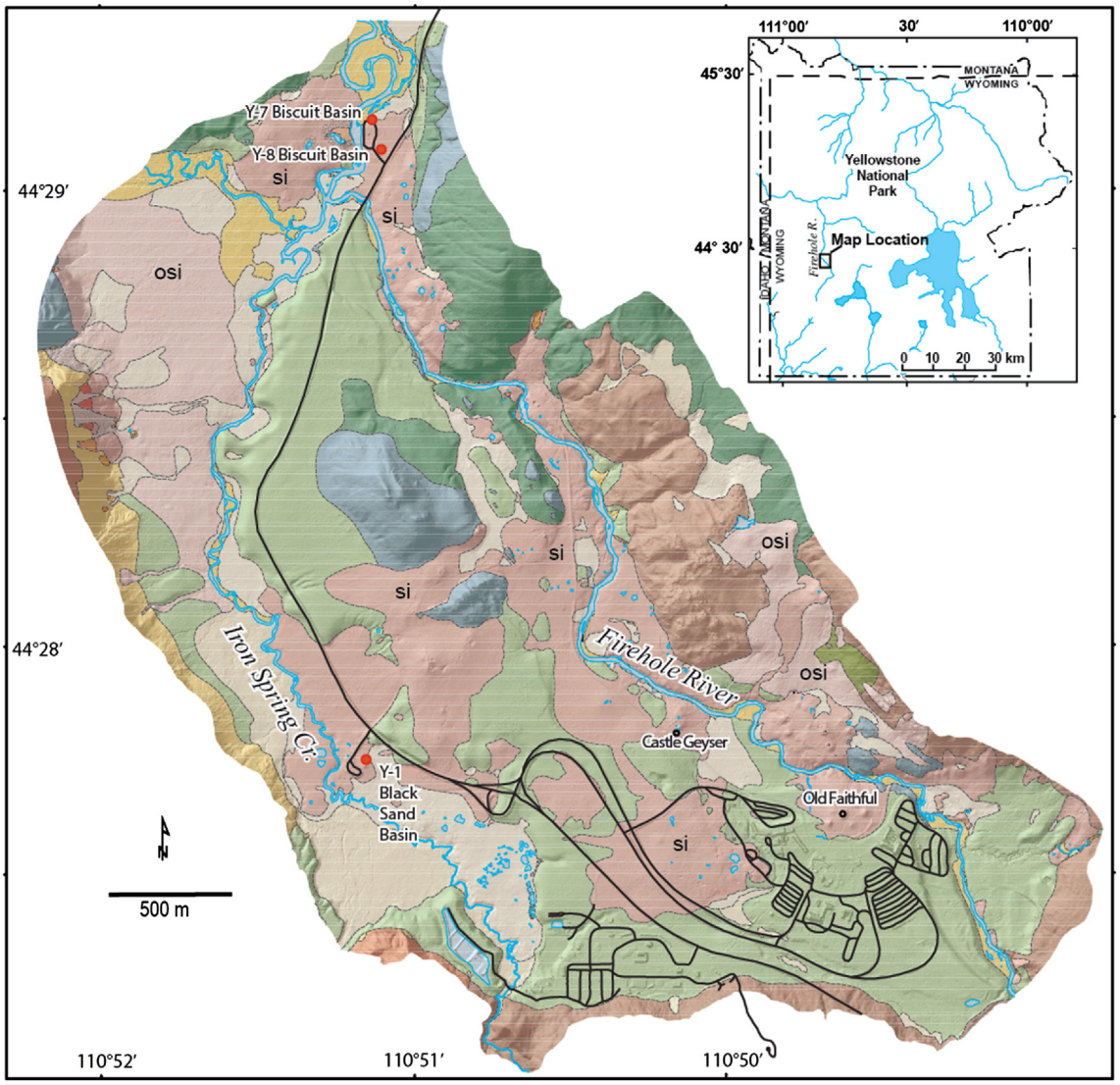

Fig. 1. Map of the Upper Geyser Basin (UGB) showing the locations of research wells Y-1 in Black Sand Basin and Y-7 and Y-8 in Biscuit Basin. Also shown are the locations of Old Faithful and Castle geysers. Black lines are roads. Geology based on Muffler et al. (1982); digital data available in Abedini et al. (2015). Labeled units are si: sinter and osi: old sinter. Green units are glacial deposits. Brown and blue are pre-70 ka rhyolite lava flows. Beige is diatomaceous silt. Light orange is sand and gravel. Geology is overlain on LiDAR topography (available at www.opentopography.org). The inset map shows the location of the Upper Geyser Basin within Yellowstone National Park.

2015). Such information is important to understand the dynamics and timing of hydrothermal flow, both on local and regional scales. If hydrothermal activity can stop for long periods of time, what might this imply about climate, tectonics, and basin-wide flow paths of thermal water?

2. Materials, methods, and results

To obtain a better record of post-glacial hydrothermal activity in the UGB, we extracted sinter samples from cores stored at the U.S. Geological Survey Core Research Center (CRC) in Denver, Colorado. The cores originate from research wells Y-1 in Black Sand Basin and Y-7 in Biscuit Basin (Fig. 1) that were drilled by the U.S. Geological Survey in 1967 to determine the physical conditions and hydrothermal mineralogy in active geothermal systems (White et al., 1975). The Y-1 well penetrated a 64-m-thick sequence of glacial and fluvial sediments before completion in the underlying rhyolite lava at 65 m. The maximum temperature at the bottom of the hole was 163.7 °C (Honda and Muffler, 1970). The first 3.7 m of core are opaline sinter or opal-A (Honda and Muffler, 1970). As in Y-1, the Y-7 core starts with opaline sinter (1.8 m thick), before passing through a series of glacial and fluvial sediments, and finishing in the Biscuit Basin (rhyolite) flow. Temperatures of ~143 °C were found at the bottom of this 74-m-deep borehole (Keith et al., 1978).

We focused our work on the very top-most opaline sinter at the tops of the two cores. We carefully inspected the cores (Fig. 2a) and regions high in visible dark organic matter were separated for later study (Fig. 2b). Studies by Honda and Muffler (1970) and Keith et al. (1978) conclude that all of the shallow sinters are entirely opal-A and have not been converted to more mature forms of silica. The core boxes are labeled for core depth, but the absolute accuracy of any individual depth may vary. Nevertheless, the relative depths of samples should be reliable. Eight samples ranging from 7 to 25 g were identified for further study. Five sinter samples came from Y-1 and three samples from Y-7, of which one did not have enough carbon for dating and is therefore not reported.

Partly crushed sinter samples were initially bathed in 1 N hydrochloric acid (HCl) for 24 h and then triply rinsed with Nanopure water. The samples were subsequently immersed in concentrated (48%) hydrofluoric acid (HF) solution for up to 48 h. Additional HF was added, as needed, to insure that all soluble material was fully dissolved. The remaining carbonaceous (non-soluble) material was triply rinsed in

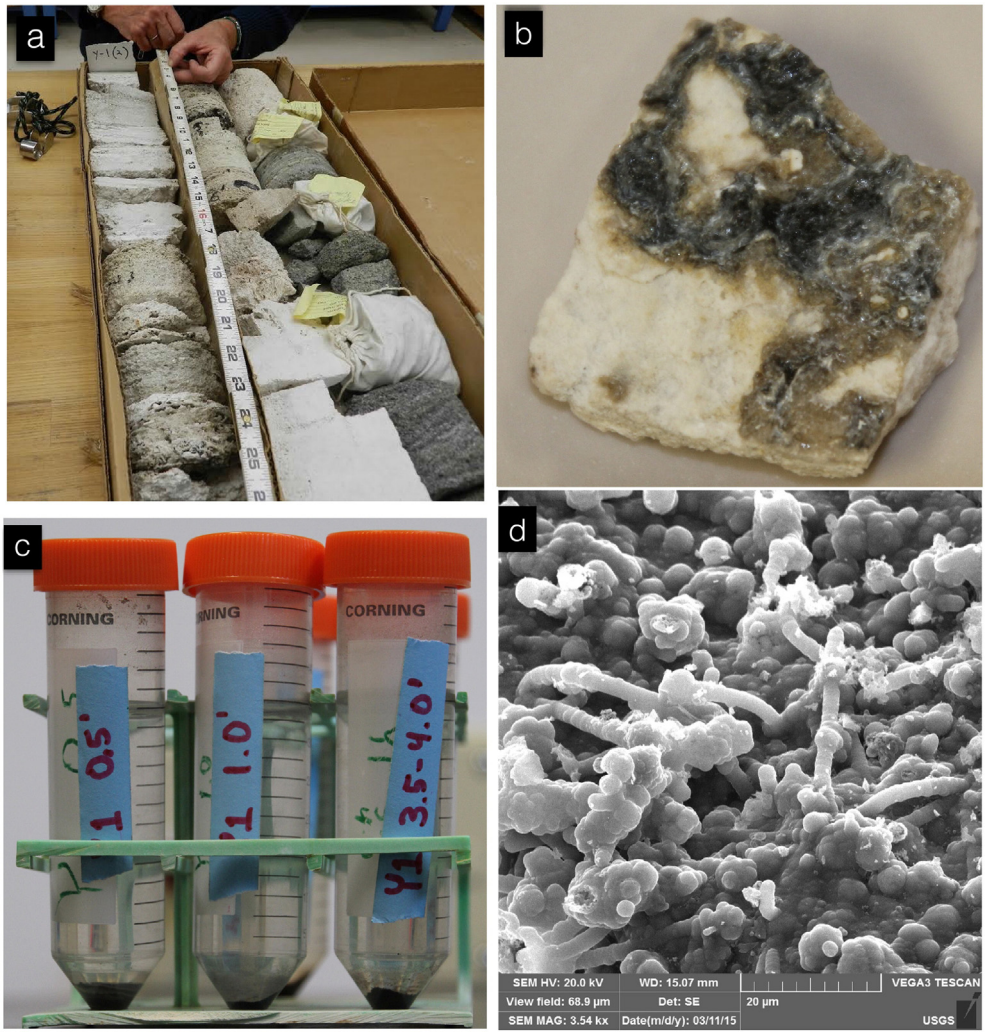

Fig. 2. Sinter samples from well Y-1 in the Upper Geyser Basin. a) Core from the upper part of the well, as provided by the repository: ruler shows inches. Top of core is upper left and lower part of core is bottom right. b) Carbon-rich sinter from a depth of 1.37 m. c) Post-processing carbon separates in Nanopure water. Denser carbon sinks to bottom of tubes (2.5 cm maximum diam.). The middle tube did not have enough material to date. The other two samples are reported in Table 1. d) Secondary-electron image of carbon-bearing sinter similar to shown in (b) with unidentified filamentous thermophilic organisms together with spherules of silica. Sample is from a depth of 1.2 m. Full scale bar at bottom is 20 μm across.

Nanopure water and centrifuged until all material sank to the bottom of the separation tube (Fig. 2c). Secondary-electron imaging and optical microscopy confirmed the presence of pollen, charcoal, and filamentous microbes (Fig. 2d), similar to observations from other studies (Jones et al., 2001; Drake et al., 2014). We did not seek to further differentiate carbon types or to separate them by size fraction (e.g., Howald et al., 2014) given the limited amounts of carbonaceous material in the small sinter samples.

Radiocarbon samples were processed at the US Geological Survey's radiocarbon dating laboratory in Reston, VA, and dated by accelerator mass spectrometry (AMS) at Lawrence Livermore's Center for Accelerator Mass Spectrometry in Livermore, CA. Samples were combusted to CO_2 and then converted to graphite over an iron catalyst using the hydrogen reduction method (Vogel et al., 1984). Two samples had a sufficient quantity of carbon collected from the combustion (>1.0 mg) to prepare a separate aliquot of CO_2 for $\delta^{13}C$ analysis in order to correct the measured ^{14}C activity for isotopic fractionation. For the other samples with insufficient carbon for $\delta^{13}C$ analysis, ranging from 0.07 to 0.7 mg, an assumed $\delta^{13}C$ value of −25‰ was used to correct the sample ^{14}C activity for fractionation (Stuiver and Polach, 1977).

The radiocarbon data in Table 1 are presented as ^{14}C years BP and as calibrated age ranges (cal years BP). In general, the samples at the tops of both cores are considerably younger (~5000 years) than the deepest samples. Two of the ^{14}C dates of the Y-1 samples are slightly out of chronological sequence. Both are samples with the smallest carbon yield and are most subject to contamination. Nevertheless, one sample (Y-1 0.76 m: calculated age of 7010 ± 60 years BP) is within error of

Table 1
Radiocarbon dates of siliceous sinter deposits from the Upper Geyser Basin.

Depth (m)	Depth (ft)	Lab ID[a]	C (mg)	$\delta^{13}C$[b]	^{14}C age[c] yr BP	±	Calibrated age[d] cal yr. BP
Y-1	**Y-1**						
0.15	0.5	WW10353	1.0	−26.0	3775	25	4084–4238
0.76	2.5	WW10176	0.1	−25	7010	60	7706–7950
1.07–1.22	3.5–4.0	WW10451	0.5	−25	6975	40	7698–7928
1.37	4.5	WW10177	0.2	−25	8500	45	9454–9543
1.52	5.0	WW10178	0.07	−25	7940	150	8422–9240
Y-7	**Y-7**						
0.24–0.30	0.8–1.0	WW10452	0.7	−25	2910	30	2961–3157
1.22	4.0	WW10354	1.0	−20.7	8025	25	8778–9010

[a] Assigned by the USGS radiocarbon dating laboratory in Reston, VA.
[b] $\delta^{13}C$ values are the assumed values according to Stuiver and Polach (1977) when given without decimal places. Values measured for the material itself are given with a single decimal place.
[c] Quoted ages are in radiocarbon years BP with 1-sigma uncertanties using the Libby half life of 5568 years and following the conventions of Stuiver and Polach (1977).
[d] Calibrations are 2-sigma ranges calculated using IntCal13 data (Reimer et al., 2013) and the CALIB 7.1 software program (Stuiver and Reimer, 1993).

the next sample below (Y-1 1.07–1.22 m: calculated age of 6975 ± 40 years BP). Similarly, Y-1 1.52 m had a very small amount of carbon (0.07 mg) available for the analysis, resulting in a relatively large analytical error (Table 1).

3. Discussion and conclusions

Overall, the obtained dates match very well with stratigraphic level in the core, and the small existing age reversal can be explained by incorporation of minor amounts of old sinter redeposited within some samples (e.g., Lynne et al., 2008). The reported counting errors are very small, but they do not account for all of the processes that could contribute to overall uncertainties. For example, reported dates could be too young if very young carbonaceous material were present in the samples due to recent fluvial redeposition, aerial deposition, or bioturbation. Old sinters have been mapped at the surface in the UGB (unit "osi" in Muffler et al., 1982), and such samples, if collected at the surface, could be affected by mixing with young carbon. Though mixing with young organic carbon is possible, it is less likely in samples obtained as downhole cores with little connection to the surface. It is easier to conceive how measured dates could be older than the actual time of deposition. This could occur if old charcoal were deposited on sinter at the time of burial, or if pieces of old sinter were disrupted and redeposited with materials forming at the surface as occurred at Steamboat Springs, Nevada (Lynne et al., 2008). Additionally, any efflux of mantle-derived ("dead") carbon could result in anomalously old ages (Evans et al., 2010), although the limited $\delta^{13}C$ data in Table 1 hints that this effect is minimal. We conclude that the silica sinters are most likely equal to or younger than our reported ages. That is, the highest sample from Y-7 was deposited at or more recently than 2910 ± 30 years BP. Additional sinter above the uppermost dated samples indicates that hydrothermal activity continued beyond that time, but stopped before the present time. The drilling sites of Y-1 and Y-7 were chosen to be near, but not on top of, active silica deposition in 1967.

For the Y-1 samples, the high proportion of ages from ~7000 to ~8500 years BP (4 of 5 samples) could indicate a higher rate of local deposition of silica at that time. Because our sampling was limited, we cannot confirm whether deposition continued prior to the last dated sample at 3775 BP. Observations at Yellowstone over the past 150 years indicate that thermal features can wax and wane in activity, with some features dying out and new ones forming. Therefore, it is possible that activity in Black Sand Basin near Y-1 was elevated from 7000 to 8500 years BP.

As noted above, our primary goal was to seek evidence for hydrothermal flow and sinter deposition between the two sets of dates for Castle Geyser (~9000 and ~1000 years BP). Combined with the published data for Castle and Old Faithful Geysers (Marler, 1956; Foley, 2006), we have evidence for some hydrothermal activity throughout the UGB during nearly all of the Holocene. We currently lack samples between ~7000 and ~4000 years BP, although additional sampling at other locations may find evidence for sinter deposition during that interval.

With the small number of available dated sinter deposits, correlation between hydrothermal activity in the UGB and regional climate patterns throughout the Holocene (Whitlock et al., 2012) is currently not feasible. Because most thermal features are transitory, with new features appearing as others vanish, establishing correlations between hydrothermal activity and climate, tectonism, and magmatism will require extensive sampling of many thermal features.

Acknowledgments

We appreciate assistance by staff of the USGS Denver Core Repository. L. Morgan and P. Shanks helped choose samples from the Y-1, Y-7, and other cores. R. Fournier, D. Foley, and H. Heasler gave encouragement and advice before and during this short project. D. Wahl provided guidance on the carbon separations with HF. L. Hayden assisted with the SEM. K. Campbell, P. Muffler, L. Morgan, and an anonymous reviewer commented on the manuscript. This study was funded by the U.S. Geological Survey Volcano Hazards Program.

References

Abedini, A.A., Robinson, J.E., Muffler, L.J.P., White, D.E., Beeson, M.H., Truesdell, A.H., 2015. Database for the geologic map of Upper Geyser Basin, Yellowstone National Park, Wyoming: U.S. Geological Survey Data Series 911, scale 1:4,800, available at http://dx.doi.org/10.3133/ds911.

Allen, E.T., Day, A.L., 1935. Hot springs of the Yellowstone National Park 466. Carnegie Institute of Washington Publication (525 pp.).

Campbell, K.A., Guido, D.M., Gautret, P., Foucher, F., Ramboz, C., Westall, F., 2015. Geyserite in hot-spring siliceous sinter: window on earth's hottest terrestrial (paleo) environment and its extreme life. Earth-Sci. Rev. 148, 44–64. http://dx.doi.org/10.1016/j.earscirev.2015.05.009.

Drake, B.D., Campbell, K.A., Rowland, J.V., Guido, D.M., Browne, P.R.L., Rae, A., 2014. Evolution of a dynamic paleo-hydrothermal system at Mangatete, Taupo Volcanic Zone, New Zealand. J. Volcanol. Geotherm. Res. 282, 19–35. http://dx.doi.org/10.1016/j.jvolgeores.2014.06.010.

Evans, W.C., Bergfeld, D., McGeehin, J.P., King, J.C., Heasler, H., 2010. Tree-ring ^{14}C links seismic swarm to CO_2 spike at Yellowstone, USA. Geology 38, 1075–1078.

Foley, D., 2006. Dating castle geyser: preliminary results and broad speculations on the geologic development of geysers and hydrothermal systems in Yellowstone national park, Wyoming, USA. Trans. Geotherm. Res. Coun. 30 (I), 413–417.

Fournier, R.O., 1985. The behavior of silica in hydrothermal solutions. Rev. Econ. Geol. 2, 45–61.

Fournier, R.O., 1989. Geochemistry and dynamics of the Yellowstone National Park hydrothermal system. Annu. Rev. Earth Planet. Sci. 17, 13–53. http://dx.doi.org/10.1146/annurev.ea.17.050189.000305.

Fournier, R.O., 2015. An explanation for how an apparent long stoppage in hot spring and geyser activity at Upper Geyser Basin, Yellowstone National Park may have come about. Geol. Soc. Am. Abstr. Programs 47 (6), 7. https://gsa.confex.com/gsa/2015RM/webprogram/Paper254901.html.

Fournier, R.O., White, D.E., Truesdell, A.H., 1976. Convective heat flow in Yellowstone National Park. Proceed. Second U.N. Symposium on the Development and Use of Geothermal Resources. U.S. Energy Res. and Dev. Admin, Washington, D.C., pp. 731–739.

Guidry, S.A., Chafetz, H.S., 2003. Anatomy of siliceous hot springs: examples from Yellowstone National Park. Wyoming. USA. Sediment. Geol. 157, 71–106. http://dx.doi.org/10.1016/S0037-0738(02)00195-1.

Honda, S., Muffler, L.J.P., 1970. Hydrothermal alteration in core from research hole Y-1, Upper Geyser Basin, Yellowstone National Park, Wyoming. Am. Mineral. 55, 1714–1737.

Howald, T., Person, M., Campbell, A., et al., 2014. Evidence for long timescale (>10^3 years) changes in hydrothermal activity induced by seismic events. Geofluids. http://dx.doi.org/10.1111/gfl.12113 (17 pp.).

Hurwitz, S., Lowenstern, J.B., 2014. Dynamics of the Yellowstone hydrothermal system. Rev. Geophys. 51. http://dx.doi.org/10.1002/2014RG000452.

Hurwitz, S., Lowenstern, J.B., Heasler, H., 2007. Spatial and temporal geochemical trends in the hydrothermal system of Yellowstone National Park: inferences from river solute fluxes. J. Volcanol. Geotherm. Res. 162, 149–171. http://dx.doi.org/10.1016/j.jvolgeores.2007.01.003.

Hurwitz, S., Hunt, A.G., Evans, W.C., 2012. Temporal variations of geyser water chemistry in the Upper Geyser Basin, Yellowstone National Park. USA. Geochem. Geophys. Geosys. 13, Q12005. http://dx.doi.org/10.1029/2012GC004388.

Jones, B., Renaut, R.W., Rosen, M.R., 2001. Taphonomy of silicified filamentous microbes in modern geothermal sinters — implications for identification. PALAIOS 16, 580–592. http://dx.doi.org/10.1669/0883-1351(2001)016<0580:TOSFMI>2.0.CO;2.

Keith, T.E., White, D.E., Beeson, M.H., 1978. Hydrothermal alteration and self-sealing in Y-7 and Y-8 drill holes in northern part of Upper Geyser Basin, Yellowstone National Park, Wyoming. U.S. Geol. Surv. Prof. Paper 1054-A (26 pp.).

Licciardi, J.M., Pierce, K.L., 2008. Cosmogenic exposure-age chronologies of Pinedale and Bull Lake glaciations in greater Yellowstone and the Teton Range, USA. Quater. Sci. Rev. 27, 814–831. http://dx.doi.org/10.1016/j.quascirev.2007.12.005.

Lowe, D.R., Braunstein, D., 2003. Microstructure of high-temperature (>73 °C) siliceous sinter deposited around hot springs and geysers, Yellowstone Park: the role of biological and abiological processes in sedimentation. Can. J. Earth Sci. 40, 1611–1642.

Lynne, B.Y., Campbell, K.A., Moore, J.N., Browne, P.R.L., 2005. Diagenesis of 1900-year-old siliceous sinter (opal-A to quartz) at Opal Mound, Roosevelt Hot Springs, Utah, USA. Sediment. Geol. 179, 249–278. http://dx.doi.org/10.1016/j.sedgeo.2005.05.012.

Lynne, B.Y., Campbell, K.A., Moore, J., Browne, P.R.L., 2008. Origin and evolution of the Steamboat Springs siliceous sinter deposit, Nevada, USA. Sediment. Geol. 210, 111–131. http://dx.doi.org/10.1016/j.sedgeo.2008.07.006.

Marler, G.D., 1956. How old is Old Faithful Geyser [Wyoming]? Am. J. Sci. 254, 615–622.

Morgan, L.A., Shanks III, W.C., Pierce, K.L., et al., 2007. The floor of Yellowstone Lake is anything but quiet—new discoveries from high-resolution sonar imaging, seismic-reflection profiles, and submersible studies. In: Morgan, L.A. (Ed.)Integrated geoscience studies in the Greater Yellowstone Area—Volcanic, tectonic, and hydrothermal processes in the Yellowstone geoecosystem: U.S. Geological Survey Professional Paper 1717, pp. 91–126.

Muffler L.J.P., White, D.E., Beeson, M.H., Truesdell, A.H., 1982. Geological map of Upper Geyser Basin, Yellowstone National Park, Wyoming. U.S. Geol. Surv. Misc. Invest. Map I-1371, scale 1:4,800. http://pubs.er.usgs.gov/publication/i1371

Reimer, P.J., Bard, E., Bayliss, A., et al., 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. Radiocarbon 55, 1869–1887.

Stuiver, M., Polach, H.A., 1977. Discussion: reporting of ^{14}C data. Radiocarbon 19, 355–363.

Stuiver, M., Reimer, P.J., 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. Radiocarbon 35, 215–230.

Vogel, J.S., Southon, J.R., Nelson, D.E., Brown, T.A., 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. Nucl. Inst. Methods 223, 289–293.

White, D.E., Fournier, R.O., Muffler, L.J.P., Truesdell, A.H., 1975. Physical results of research drilling in thermal areas of Yellowstone National Park. Wyoming. U.S. Geol. Surv. Prof. Pap. 892 (70 pp.).

Whitlock, C., Dean, W.E., Fritz, S.C., Stevens, L.R., Stone, J.R., Power, M.J., Rosenbaum, J.R., Pierce, K.L., Bracht-Flyr, B.B., 2012. Holocene seasonal variability inferred from multiple proxy records from Crevice Lake, Yellowstone National Park, USA. Palaeogeogr. Palaeoclimatol. Palaeoecol. 331, 90–103. http://dx.doi.org/10.1016/j.palaeo.2012.03.001.