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B.Y. LYNNE[1] K.A.CAMPBELL[1] P.R.L. BROWNE[1]
Scientist, Department of Geology, University of Auckland, NZ.

B. JAMES[2]
Engineer, Department of Engineering, University of Auckland, N.Z.

J.N. MOORE[3]
Scientist, Energy and Geoscience Institute, University of Utah, U.S.A.

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[1]Univeristy of Auckland, Geology Department, Chemistry Building, 23 Symonds Street, Auckland, N.Z.
Ph. +64-9-373-7599

[2]University of Auckland, Faculty of Engineering, Research Centre for Surface and Materials Science, Symonds Street, Auckland, N.Z.
Ph. +64-9-373-7599

[3]Energy and Geoscience Institute, Department of Civil and Environmental Engineering, 423 Wakara Way, Suite 300, Salt Lake City, Utah 84108, U.S.A.
Ph. +1-801-585-6931

SILICEOUS SINTER DIAGENESIS: ORDER AMONG THE RANDOMNESS

B.Y. LYNNE[1], K.A. CAMPBELL[1], B. JAMES[2], P.R.L. BROWNE[1], J. MOORE[3],
[1]Department of Geology, University of Auckland, New Zealand
[2]Department of Engineering, University of Auckland, New Zealand
[3]Energy and Geoscience Institute, University of Utah, U.S.A.

SUMMARY – Sinters form where near-neutral-pH, alkali chloride waters discharge at the surface. As these waters cool, silica precipitates, coating all biogenic and abiogenic components. Hydrothermal systems are contenders for having hosted early life on Earth. Therefore sinters can be used as extreme-environment analogs in the search for early biosignals. However, they experience diagenetic changes that can modify original environmental signatures. Sinters undergo diagenesis through a 5-step series of phase changes, from opal-A to opal-A/CT to opal-CT to opal-C to quartz (± moganite). Three sinters that preserve the opal-A to quartz diagenetic sequence are: (1) < 11,500 years BP ± 70 years sinter at Steamboat Springs, Nevada, U.S.A, (2) < 1900 ± 160 years BP Opal Mound sinter at Roosevelt Hot Springs, Utah, U.S.A, and (3) 456 ± 35 years BP deposit at Sinter Island, Lake Ohakuri, Taupo Volcanic Zone, New Zealand. Crystallographic, mineralogic and morphologic transformations during diagenesis were tracked using electron backscatter diffraction, X-ray powder diffraction, and scanning electron microscopy. Morphological transformations involve repetitive growing and shrinking of silica particles from the micron- to nano-meter scales. The alignment of morphological features in the siliceous sinter matrix during diagenesis is predetermined by crystallography and represents future crystal-face growth directions. Crystallographic and morphologic indicators of quartz manifest in all precursor silica phases except opal-A. All deposits followed nearly identical diagenetic pathways, with time being a variable in the progress toward stable quartz. Diagenesis modifies original environmental signatures by obscuring primary biotic and abiotic inclusions. Thus, in order to accurately identify biosignals in ancient hot-spring deposits it is necessary to recognize the diagenetic effects imprinted on fossil sinter deposits.

1. INTRODUCTION

Siliceous sinter forms where hot alkali chloride waters discharge and cool at the Earth's surface. As temperatures drop, silica deposits on all exposed surfaces, including microbes, insects, pollens, plants and older sinter surfaces. All these components become entombed, silicified and fossilized in sinters, making them excellent archives of paleoenvironmental conditions. However, sinters undergo a five-step series of mineralogic, morphologic and crystallographic changes during diagenesis. Freshly deposited sinter comprises non-crystalline opal-A, which transforms to non-crystalline opal-A/CT, then to para-crystalline opal-CT, opal-C and eventually to micro-crystalline quartz (Lynne et al., 2005). This process was previously estimated to take ~ 10,000 years or longer (Herdianita et al., 2000a). However, more recent research shows that the time required for opal to transform to quartz differs for each deposit (Rodgers et al., 2004, Lynne et al., 2005, 2006). Various environmental conditions can influence the depositional and post-depositional changes experienced by sinter accumulations. Lynne and Campbell (2004) summarized previous studies that have examined silica depositional processes in hot spring environments. This study is the first to deconstruct the sinter diagenetic continuum into its crystallographic components. Three sinter deposits were analyzed: Sinter Island, New Zealand; Opal Mound, Utah, U.S.A; Steamboat Springs, Nevada, U.S.A.

2. METHODS

2.1 ^{14}C ages of sinter

The three sinters were dated by calibrated ^{14}C analysis of entombed plant and pollen fragments using accelerator mass spectrometry (AMS) at the Rafter Radiocarbon Laboratory, GNS Ltd., Lower Hutt, New Zealand. Extraction methods are described by Lynne et al. (2003).

2.2 X-ray powder diffraction (XRPD) analysis

XRPD analysis is the principal technique used to determine silica phase mineralogy, as well as to compare the degree of mineralogical maturation among samples. Operating conditions and data analysis procedures follow those outlined in Herdianita et al. (2000b). The full width at half maximum (FWHM) of the XRPD trace is used as a guide to the degree of silica phase maturation. The FWHM value decreases with increasing mineralogical maturation.

2.3 Scanning electron microscopy (SEM)

SEM is used to trace morphological changes in the siliceous matrix during sinter diagenesis. Sample preparation and operating procedures are outlined in Lynne et al. (2005).

2.4 Electron backscatter diffraction (EBSD)

EBSD was used to track changes in crystallinity during sinter diagenesis. Samples were highly polished, placed inside the SEM and inclined at angles of ~ 70 º to the horizontal. The electrons of the primary beam were diffracted by the crystal planes of the sample. The resulting electron backscatter patterns were captured by a low-light sensitive camera. Indexing the width of the diffraction bands and their relative angles provides information on the crystallography of the specimen. EBSD was performed using a TSL EBSD system equipped with a Digiview slow-scan CCD camera, a TSL OIM 3 Data collection program and a TSL OIM Analysis processor.

3. RESULTS

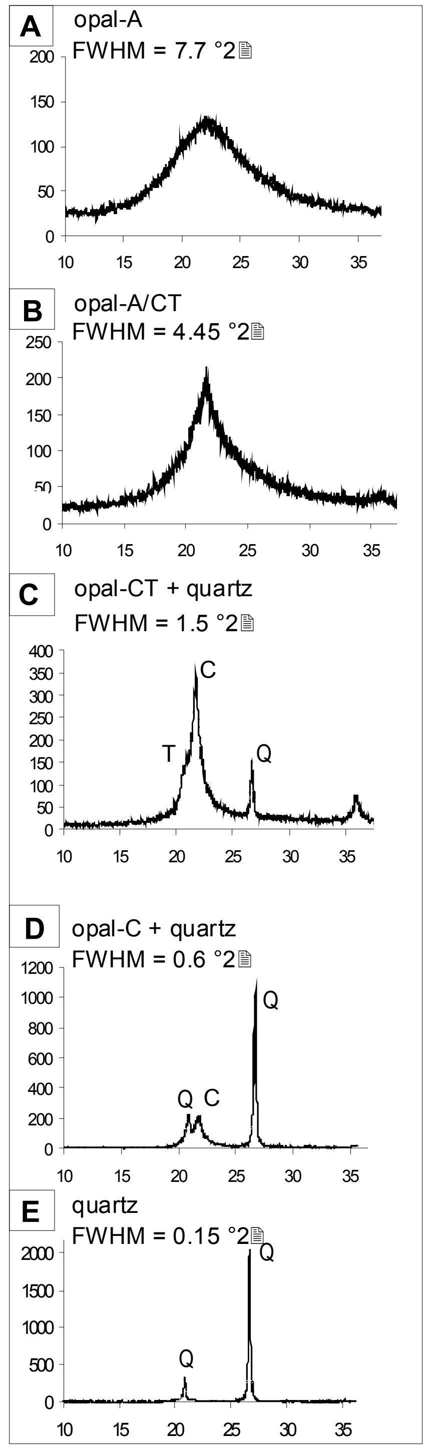
3.1 ^{14}C ages of sinter

Two sinter samples from the Opal Mound, Roosevelt Hot Springs, Utah, one consisting of opal A and the second containing quartz, yielded ages of 1630 ± 90 years BP and 1920 ± 120 years BP respectively. An age of 456 ± 35 years BP was obtained on sinter with opal-CT from Sinter Island, New Zealand. Sinter from Steamboat Springs, Nevada, comprising opal-CT and opal-CT + quartz yielded ages of 6283 ± 60 years BP and > 11,493 ± 70 years BP, respectively.

3.2 Mineralogical transitions

The three sinter deposits displayed all five silica phase transitions. Transformations from one silica phase to the next were incremental, and diagenetic changes were recorded by a progressive sharpening of the XRPD broadband and a decrease in FWHM values (Figure 1). Sinter from the three deposits had similar FWHM values in the following ranges: opal-A, 8.0 – 6.0 º2Θ; opal-A/CT, 6.0 – 3.5 º2Θ; opal-CT, 2.5 – 1.0 º2Θ; opal-C, 0.9 – 0.7 º2Θ; quartz, 0.4 – 0.1 º2Θ.

Figure 1: Representative X-ray powder diffraction traces of siliceous sinter from the Opal Mound, Roosevelt Hot Springs, Utah, showing the progression of silica phases during sinter diagenesis. (A) Opal-A. (B) Opal-A/CT. (C) Opal-CT + quartz. (D) Opal-C + quartz. (E) Quartz.



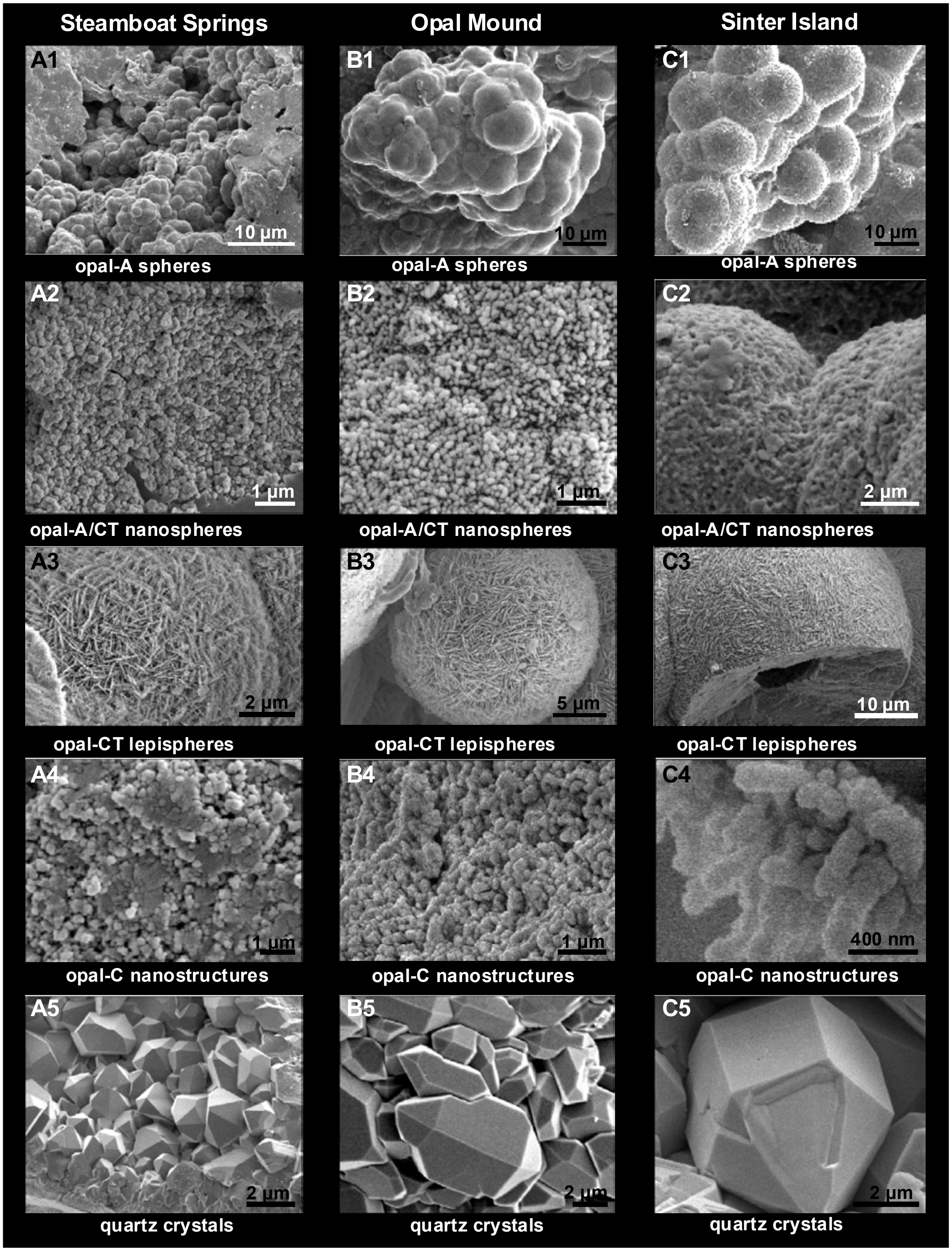


Figure 2: Comparative morphologies of sinter matrix for each silica phase from the three deposits of this study, from freshly deposited (1) to most mature (5). (A1 - A5) Steamboat Springs, Nevada, U.S.A. (B1 - B5) Opal Mound, Roosevelt Hot Springs, Utah, U.S.A. (C1 - C5) Sinter Island, Taupo Volcanic Zone, New Zealand.

3.3 Morphological transitions

Morphological modifications during sinter diagenesis were captured by SEM images. Alternating, micro- to nano-sized particle changes were revealed (Figure 2). Comparison of morphological transformations among the deposits shows that the opal-A to opal-CT step is almost identical for all three sinters; however, the shift from opal-CT to quartz differs in the arrangement of the opal-C nano-structures (Figure 3).

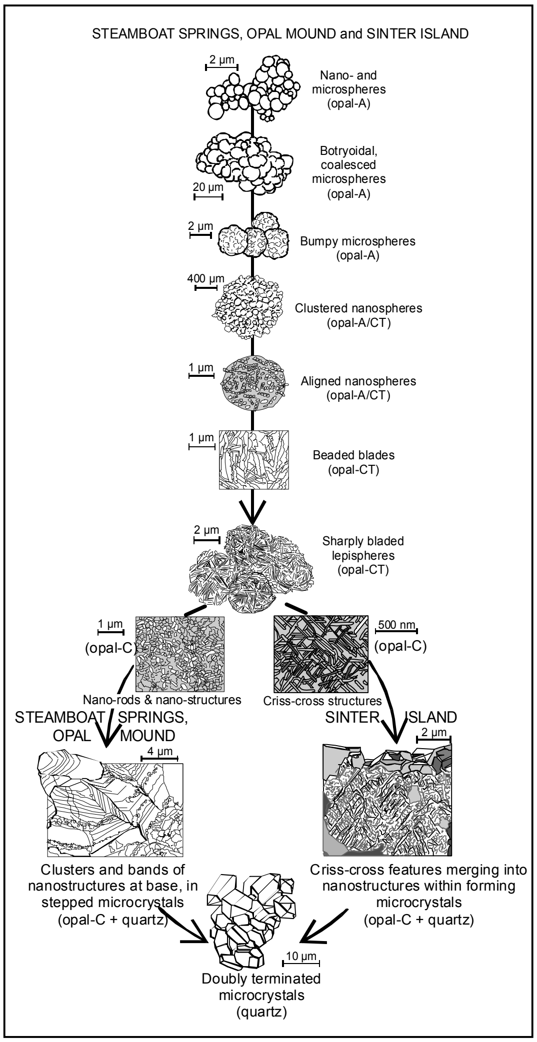


Figure 3: Schematic diagram summarising morphological changes accompanying silica phase transitions from opal-A to quartz.

3.4 Crystallographic transitions

EBSD analysis allowed detailed tracking of the crystallographic changes that accompanied the mineralogical and morphological transformations from opal-CT to quartz (Figure 4). Immature sinter samples (opal-A and opal-A/CT) were not crystalline enough to produce any EBSD results. Quartz has crystallographic axes at; x=60º, u=120º, y=0º and a z-axis at 90º to these three. The EBSD results showed that the axes of the pre-quartz silica phases, opal-CT and opal-C, differ slightly from the ideal values. Axes of diagenetic quartz from Sinter Island are at x=68º, u=136º, y=0º. Those from the Opal Mound are at x=48º,

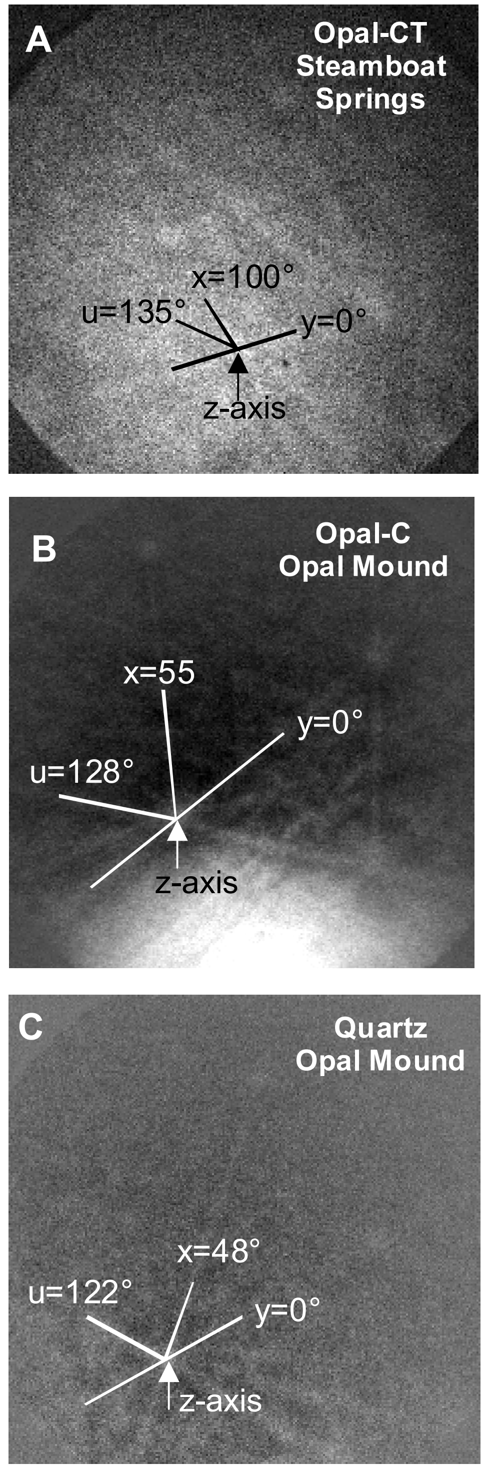


Figure 4: EBSD images displaying crystal axes within samples.

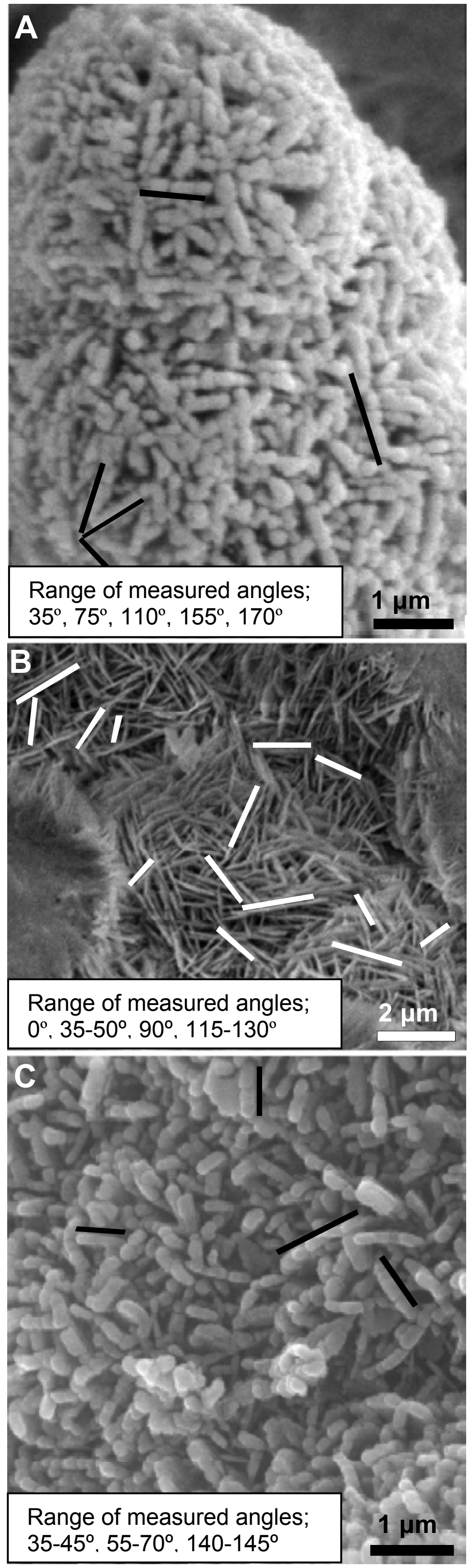
u=122º, y=0º; and those from Steamboat Springs are at x=80º, u=140º, y=0º. This range of crystallographic angles suggests that diagenetic changes occur gradually.

SEM images of all silica phases, except opal-A, revealed aligned morphological features that have preferred orientations. The orientations of these features were measured with respect to a horizontal axis arbitrarily assigned to 0º (Figure 5). A limited range of angles were recorded for all the aligned features. Crystal faces form at 90º to the crystallographic axes. Comparison of orientations of aligned morphological features and EBSD crystallographic axes showed that most of the morphological features of a given phase were oriented close to 90º to the measured crystallographic axis. Therefore, the apparent randomness of opal-C aligned nanostructures and blades of opal-CT are actually controlled by crystallography, and represent the orientations of future crystal faces. A more detailed assessment of the crystallographic relationships is presented in Lynne et al. (in review).

4. DISCUSSION AND SUMMARY

Sinter deposits from the Opal Mound, Roosevelt Hot Springs, Utah, Steamboat Springs, Nevada, U.S.A., and Sinter Island, New Zealand, have captured the entire diagenetic continuum of silica phase changes from opal-A to quartz. Sinter diagenesis consists of a progression of linked mineralogical, morphological and crystallographic transformations. Two morphological pathways are identified, with each pathway consisting of multiple alternating changes from nano- to micro-meter sized particles. Regardless of the morphological pathway, each deposit experienced similar mineralogical and crystallographic changes. The new application of EBSD to sinter diagenesis demonstrates that crystallographic and morphologic signatures of quartz are imprinted on all pre-quartz phases, except opal-A. Opal-CT and opal-C samples adopted crude crystallographic axes of quartz even before quartz had formed. The arrangement of blades within opal-CT lepispheres and opal-C nanostructures is not random, but occurs at ~ 90º to crystal axes. Therefore, we conclude the arrangement of aligned morphological features represent the incipient orientations of future quartz crystal faces. It is likely that the observed repetitive orientation of aligned nanospheres in opal-A/CT also represent orientations of future quartz faces. This study shows that crystallographic changes happen prior to or concurrently with mineralogic changes and that diagenesis is destined to proceed only as quickly as crystallographic changes occur.

Figure 5: SEM images show the alignment of morphological features. (A) opal-A/CT, Sinter Island. (B) Opal-CT, Steamboat Springs. (C) Opal-C, Opal Mound, Roosevelt Hot Springs.



EBSD showed that throughout mid- to late-diagenesis (opal-C to quartz), angular relationships among crystallographic axes are close to the ideal 60º angle. The tracking of mineralogical changes using XRPD also revealed phase changes as silica lattice ordering increased.

Sinters are genetically important hot-spring deposits because they can preserve evidence of paleoenvironments associated with surface hydrothermal discharges. All sinter deposits eventually undergo diagenesis, which can affect the preservation potential of encapsulated biological components. Therefore, an understanding of diagenesis is necessary to distinguish primary or post-depositional diagenetic overprints.

This research applied new techniques to study silica phase modifications in sinters, and these methods can be used in other areas of research. Silica phase diagenetic transformations similar to those in sinters also occur during wood petrification, siliceous marine sedimentation and burial, sinter residue diagenesis and desert varnish formation. Therefore, these techniques can be utilized across a broad range of scientific investigations where silica deposition and diagenesis occur.

5. REFERENCES

Herdianita, N.R., Browne, P.R.L., Rodgers, K.A., and Campbell, K.A. (2000a). Mineralogical and textural changes accompanying ageing of silica sinter: *Mineralium Deposita,* Vol. 35, 48-62.

Herdianita, N.R., Rodgers, K.A., and Browne, P.R.L. (2000b). Routine instrumental procedures to characterise the mineralogy of modern and ancient silica sinters: *Geothermics,* Vol. 29, 65-81.

Lynne, B.Y., Moore, J., Browne, P.R.L., and Campbell, K.A. (2003). Age and mineralogy of the Steamboat Springs silica sinter deposit, Nevada, U.S.A: A preliminary report of core SNLG 87-29: *Proceedings 25th NZ Geothermal Workshop,* 65-70.

Lynne, B.Y., and Campbell, K.A. (2004). Morphologic and mineralogic transitions from opal-A to opal-CT in low-temperature siliceous sinter diagenesis, Taupo Volcanic Zone, New Zealand: *Journal of Sedimentary Research,* Vol. 74, 561-579.

Lynne, B.Y., Campbell, K.A., Moore, J. and Browne, P.R.L. (2005). Diagenesis of 1900-year-old siliceous sinter (opal-A to quartz) at Opal Mound, Roosevelt Hot Springs, Utah, U.S.A: *Sedimentary Geology,* Vol. 119, 249-278.

Lynne, B.Y., Campbell, K.A., Perry, R.S., Moore, J. and Browne, P.R.L. (2006). Acceleration of sinter diagenesis in an active fumarole, Taupo Volcanic Zone, New Zealand: *Geology,* Vol. 34(9), 749-752.

Lynne, B.Y., Campbell, K.A., James, B., Moore, J.N., and Browne, P.R.L. Tracking crystallinity in siliceous hot-spring deposits. *American Journal of Science,* in review.

Rodgers, K.A., Browne, P.R.L., Buddle, T.F., Cook, K.L., Greatrex, R.A., Hampton, W.A., Herdianita, N.R., Holland, G.R., Lynne, B.Y., Martin, R., Newton, Z., Pastars, D., Sannazarro, K.L., and Teece, C.I.A. (2004). Silica phases in sinters and residues from geothermal fields of New Zealand: *Earth Science Reviews,* Vol. 66, 1-61.

6. ACKNOWLEDGEMENTS

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