X-RAY CHARACTERISATION OF SILICEOUS SINTER FROM STEAMBOAT SPRINGS AND ROOSEVELT GEOTHERMAL FIELDS, USA

Ilyas Qasim[1], Bridget Y. Lynne[2]

[1]School of Environment, Faculty of Science, the University of Auckland, New Zealand

[2] Department of Engineering Science, the University of Auckland, New Zealand.

ilyas.qasim@auckland.ac.nz

Keywords: *X-ray, XRD, XRF, iTRAX, siliceous sinter, geochemical analysis, phase identification, elemental analysis*

ABSTRACT

A combination of different X-ray techniques was used to achieve a comprehensive understanding on siliceous sinters (hot spring rocks) from Steamboat Springs, Nevada, USA, and Roosevelt, Utah, USA. The iTRAX Core Scanner was used to provide in-position geochemical information both qualitatively and quantitatively. By using elemental correlation analysis with the iTRAX results, it was possible to identify mineral phases, examine the various elements and assess their effect on the sinter mineralogy. X-ray diffraction (XRD) was used to examine mineralogy and crystallinity of the siliceous sinters. The information obtained from iTRAX analysis extended and reinforced the XRD results, as XRD is best suited to identify and quantify the mineralogy of crystalline compounds. Further, Wavelength Dispersive X-ray Fluorescence (WD-XRF*)* was used for the precise elemental analysis. The methodology of combining multiple X-ray techniques provides meaningful information in solving environmental puzzles such as fluid chemistry and the development of complex sinter mineralogy, common in geothermal systems around the world.

1. X-RAY TECHNIQUES AND SILICEOUS SINTERS

1.1 INTRODUCTION

1.1 Introduction

Powder X-ray diffraction (PXRD) is primarily a crystal structure characterisation technique developed by the father and son Noble prize winners - Braggs a century ago (Anders Liljas, 2013). Using the structural fingerprints acquired through XRD measurement, it's possible to identify phases in a measured sample, and quantify each crystalline phase. Hence the method has been developed for use in many disciplines such as geology, polymeric, environmental, pharmaceutical, and forensic sciences (Das *et al.* 2014). XRD is a very powerful technique that provides quantitative and qualitative analysis of compounds that cannot be measured by other means, however, as for amorphous materials it can provide only limited information.

X-ray Fluorescence (XRF) spectrometry is an elemental analysis technique that can identify and quantify elements (usually good for elements with atomic number 11 and above) in crystalline and non-crystalline materials. Modern XRF instruments are capable of analysing solid, liquid, and thin film samples for both major and trace elements (up to ppm level). There are many different types of XRF available, including portable X-ray Fluorescence spectrometer (p-XRF), Energy dispersive X-ray Fluorescence (ED-XRF), and Wavelength Dispersive X-ray Fluorescence (WD-XRF) spectrometer. The latter one is generally preferred for scientific research as it can provide higher resolution and higher accuracy data due to fewer spectral overlaps and lower background intensities.

The iTRAX Core Scanner (Croudace et al. 2006) provides in-situ semi-quantitative (originally presented as counts) elemental analysis and results affected by sample properties such as cracks and uneven surfaces, grain size, compaction, organic content and moisture etc. It is a non-destructive technique that simultaneously provides optical and X-radiographic images, and elemental profiles obtained by XRF that are invaluable for guiding sample and method selection for further (destructive) analyses.

In this paper, attempts were made to obtain rather comprehensive geochemical information on siliceous sinters by effective combination of these three X-ray techniques.

Siliceous sinters are common in geothermal areas where alkali chloride water discharges at the surface after equilibrating with the underlying rocks at temperatures >175 °C (Fournier and Rowe, 1966). The silica carried in the fluid is initially deposited as amorphous opal-A when alkali chloride water discharges and cools to temperatures below 100 °C. Over time, the amorphous opal-A silica transforms into opal-A/CT then to para-crystalline opal-CT +/- opal-C and eventually to microcrystalline quartz (Herdianita et al., 2000). Such transitions can occur in deposits with little or no burial. Trace elements may also be incorporated into the sinter if the fluid is trace element-rich.

1.2 Samples and Geological settings

A total of seven trace element-rich sinter samples representing a range of silica phases from Steamboat Springs (Lynne et al., 2008) and Opal Mound (Lynne et al., 2005) were examined using three X-ray analytical techniques. Four of the Steamboat Springs sinters are cored samples with 19'4" representing a shallower cored sample and 33'3" representing a deeper cored sample. All other samples were from surface outcrops (see Table 1). X-ray Diffraction, X-Ray Fluorescence and iTRAX analyses were undertaken on seven trace element-rich sinter samples to determine their mineralogy and composition.

2. METHODS

Instrument Settings and Experimental Procedure

All samples were first scanned for optical image, X-ray radiographic image and XRF using the iTRAX Core Scanner from COX Analytical (Croudace *et al.* 2006). An example of samples scanned on iTRAX Core Scanner is given in Fig.1.

The iTRAX Core Scanner from COX Analytical (Croudace *et al.* 2006) was used to obtain X-ray image and XRF scan for all samples. X-ray radiographic and XRF scans with 200

Table 1: Location, age and sample number of sinters analysed.

Location	Sample ID	Age
Steamboat Springs cored sample	19'4"	
Steamboat Springs cored sample	21'2"	
Steamboat Springs cored sample	26'8"	8684±64 years (Lynne et al. 2008)
Steamboat Springs cored sample	33'3"	11,493±70 years (Lynne et al. 2008)
Steamboat Springs surface sample	H2	
Opal Mound, Roosevelt surface sample	R1A	1630+/-90 years (Lynne et al. 2005)
Opal Mound, Roosevelt surface sample	R6B2	1630+/-90 years (Lynne et al. 2005)

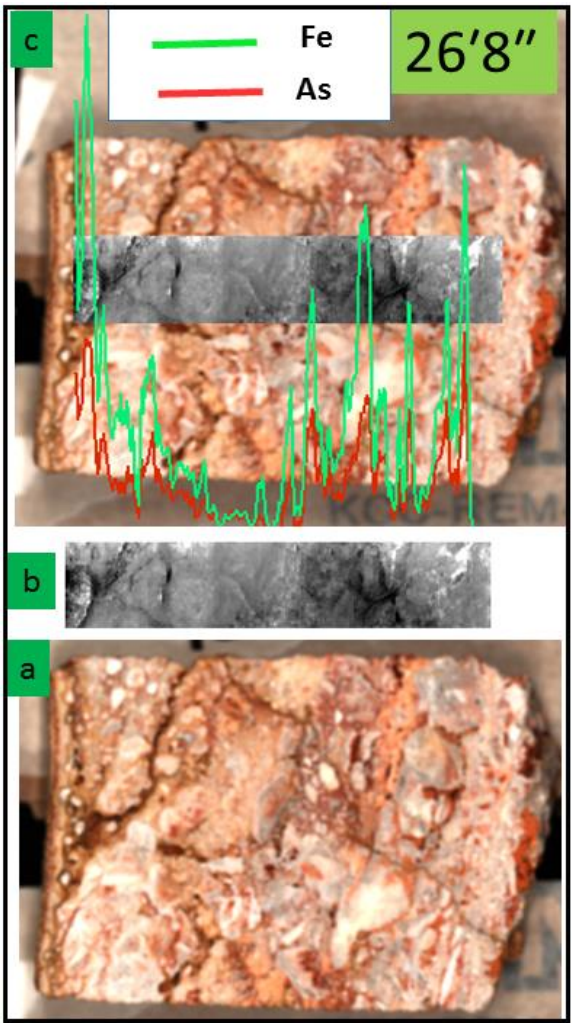

Fig. 1. Sample 26'8" scanned on iTRAX Core Scanner (a) Optical image, (b) radiographic image, (c), overlay image to show XRF scanning positions (grey area) and elemental distribution/abundance for selected elements.

micron step size were performed under Molybdenum (Mo) X-ray tube with a working voltage of 50kV/40mA and 30mA/55 kV respectively.

Powder XRD pattern was collected using PANalytical's Empyrean Powder X-ray diffractometer (at the University of Auckland), equipped with a Cu anode X-ray tube using mono-chromatid Cu Kα X-rays at operating voltage and current 45kV/40mA. Data was collected from 2theta = 10°~80° with step size 0.0131°.

In order to determine bulk concentrations, major and trace element analyses were performed using a PANalytical's Axios 1 kW wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer in the X-ray Centre at the University of Auckland. Samples were crushed to a fine powder using an automated tungsten ring mill. To determine loss on ignition (LOI), approximately 1.5 g of powdered sample was weighed and heated at 900 °C for 16 h. To gain higher resolution for trace elements, sample flux ratio of 1:2 was used to make fused dead (glass disk) for the XRF measurements. Well mixed 3.5000 grams of ring milled powder sample and 7.000 grams of X-ray fluxing agent (12:22 - lithium tetraborate 35.3%/Lithium metaborate 64.7%) were added into Pt–Au crucible for fusing glass discs using a PANalytical Eagon-2 at 1000 °C. Fusion bead (glass disk) was obtained for each sample and XRF measurements were performed on the disk - the solid solution of each sample.

3. RESULTS

Seven samples were chosen to represent a range of silica phases present within trace element-rich sinters from two locations (see Table 2). Samples revealed opal-A, opal-A/CT, opal-CT and quartz silica phases with Full Width at Half Maximum (FWHM) values that ranged between 6.8 and 0.1 °2θ (see Table 2).

Table 2: Silica phase mineralogy as determined by XRD.

Location	**Sample ID**	**Mineralogy**	**FWHM value (°2θ)**
Steamboat Springs	19'4"	Opal-A	6.1
Steamboat Springs	21'2"	Opal-A/CT	4.9
Steamboat Springs	26'8"	Opal-A/CT	4.1
Steamboat Springs	33'3"	Opal-CT	2
Steamboat Springs	H2	Quartz	0.1
Opal Mound	R1A	Opal-A	6.8
Opal Mound	R6B2	Opal-A/CT	3.5

Well-defined XRD peaks were observed for the quartzose sinter H2 only; FWHM value = 0.1°2θ degrees from Steamboat Springs (Fig. 4). The XRD profile fitting using HighScore Plus suite (http://www.panalytical.com/Xray-diffraction-software/HighScore.htm) revealed mineralogy which are very well supported by both our XRF and iTRAX results. The XRD pattern for sample H2 revealed that the vast majority of the crystalline phases in sinter sample H2 is

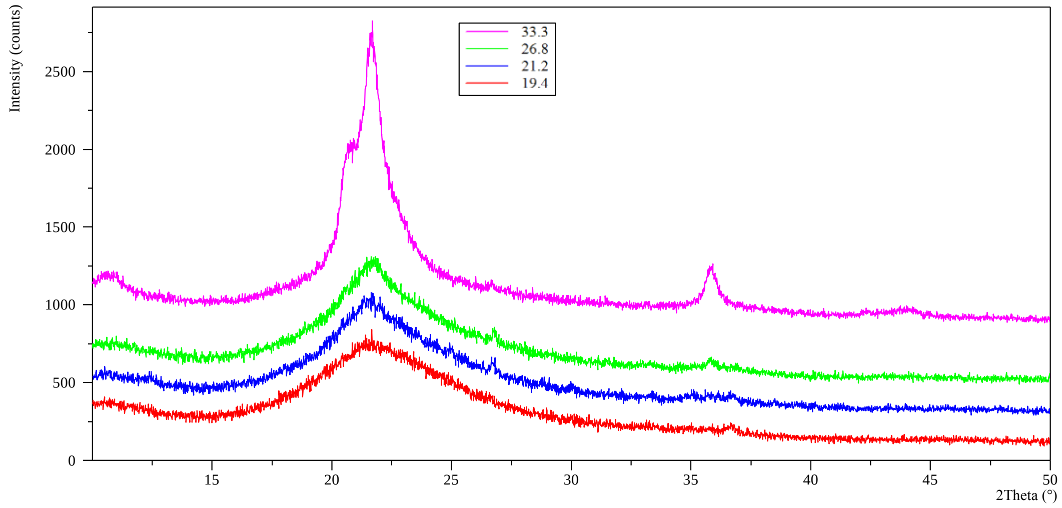

Fig. 2: XRD profiles for cored siliceous sinter samples from Steamboat Springs, Nevada, USA. An increase in silica phase maturation is shown with increasing depth from opal-A (19’4” FWHM value = 6.1 °2θ) to opal-A/CT (21’2” FWHM value = 4.9 °2θ; 26’6” FWHM value = 4.1 °2θ) to opal-CT (33’3” FWHM value = 2 °2θ).

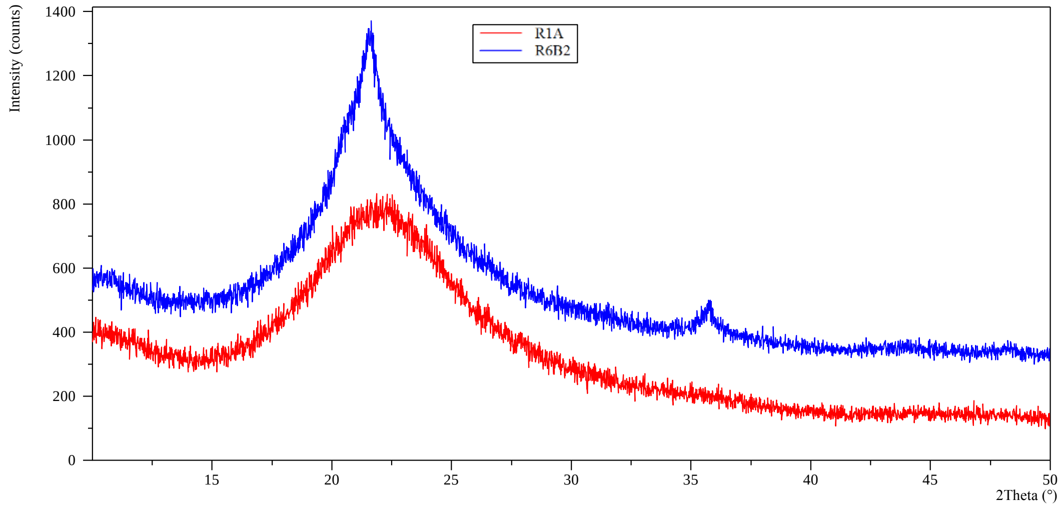

Fig. 3: XRD profiles for surface siliceous sinter samples from Opal Mound, Utah, USA. Sample R1A shows a typical opal-A broadband with a FWHM value of 6.8 °2θ and sample R6B2 consists of opal-A/CT with a FWHM value of 3.5 °2θ.

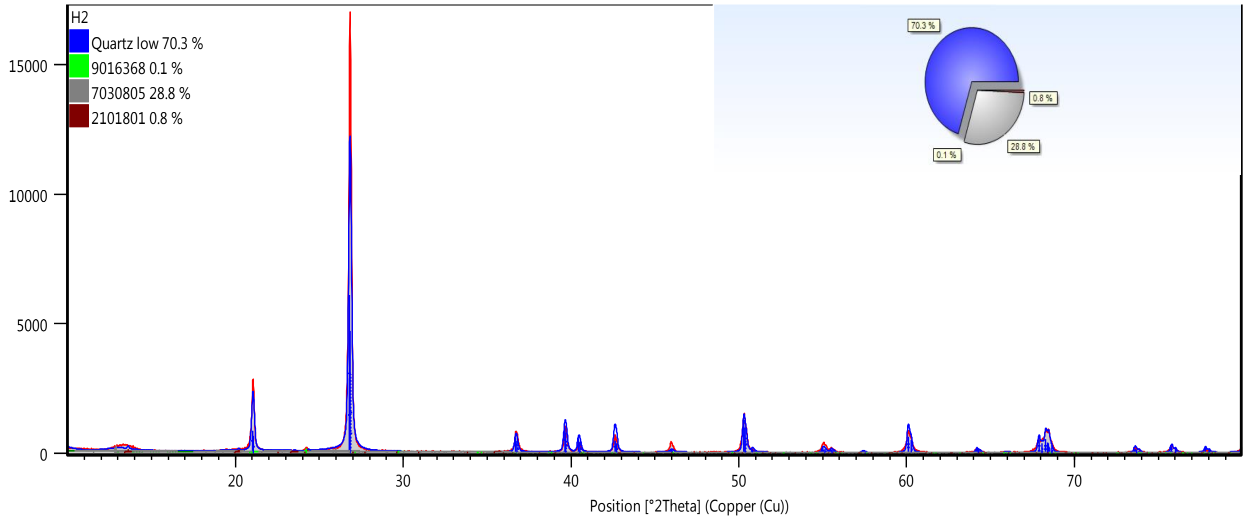

Fig. 4. Powder XRD profile and calculated bulk mineralogy for sinter sample H2 from Steamboat Springs

Table 3. Bulk mineralogy for quartzose sinter sample H2 determined using HighScore Plus analysis. (Compound name/IDs were from COD XRD database-2014 during HighScore Plus analysis)

Compound name/ID	Quartz	7030805	9216368	2101801
Chemical Formula	SiO_2	$Si_{36}O_{72}$	$Mg_{4.0}Si_{4.0}(OH)_{24}$	$As_6C_{36}O_{36}H_{54}$
Weight %	70.3	28.8	0.1	0.8%
Crystal structure (Space group)	hexagonal *(P 31 2 1)*	Orthorhombic *(P 21 21 21)*	Orthorhombic *(C m c 21)*	Hexagonal *(R 3 c)*

Table 4. XRF results for the major ((in weight %) and trace (in ppm) elements present in all seven sinter samples (L.O.I – Loss on Ignition, in weight %).

Sample	L.O.I	SiO_2	Fe_2O_3	Al_2O_3	As (ppm)	S (ppm)
19’4”	7.24	90.11	1.79	0.45	557	353
21’2”	7.41	86.76	2.23	1.7	793	798
26’8”	7.32	89.89	1.05	0.92	218	431
33’3	7.4	90.84	0.35	0.27	173	215
R1A	8.45	90.47	0.06	0.12	1962	971
R6B2	7.28	92.18	0.02	0.1	153	384
H2	1.61	97.36	0.13	0.04	18	-

quartz and that the majority of the quartz is hexagonal but some quartz crystals are orthorhombic (see Table 3).

All samples were scanned with the iTRAX core scanner to determine their elemental composition. An example of the iTRAX core scanner result for Steamboat Springs sinter sample is shown in Figure 1. The iTRAX data shows the locations of the various trace elements within the sample. For example, Figure 1c shows the darker brown/red bands within the sample are related to high arsenic concentrations as well as containing reasonable amounts of iron. Arsenic and iron concentrations are lower in the orange coloured bands. As seen from the figure, the linear correlation between Fe and As concentrations is consistent in throughout the scanned surface, indicating that these two elements present as a compound. Our XRF results show all samples were dominantly silica with significant concentrations of iron, arsenic and sulphur (Table 4).

For the Steamboat Springs sinters located in Nevada, iron, is significantly higher (>1 weight percent) in the shallower cored samples (above 26’8”), while in the deeper cored samples the amount of iron has reduced significantly to 0.35 weight percent. Arsenic and sulphur is also highest in the three shallowest samples (above 26’8”), but the sinter still contains relatively high amounts of arsenic and sulphur in the deeper 33’3” sample, at >173 weight percent and 215 weight percent, respectively. The mineralogically more mature quartz sinter reveals minimal iron, arsenic and no sulphur.

The two sinter samples from Opal Mound in Utah, provide examples of coloured sinters with different trace element compositions to those from Steamboat Springs, Nevada.

4. DISCUSSION

While sinters from Steamboat Springs, Nevada, USA and Opal Mound, Utah, USA are both strongly coloured, their elemental compositions differ. This demonstrates the variability of discharging alkali chloride fluid chemistry within the two geothermal fields (i.e., regional scale).

Furthermore, localised differences in discharging fluid composition over time is revealed in the Steamboat Springs sinter where there is a significant difference in trace element composition between the shallower cored sinters (26’8” and above) and the deeper sinter sample (33’3”). This indicates a time during the history of the geothermal field when the discharging alkali chloride fluid changed from Fe-As-S-poor to Fe-As-S-rich fluid. Based on the dates determined for the sinter, a change in fluid composition occurred sometime between 11,493 (trace element-poor fluid) and 8684 years ago (trace element-rich fluid).

The XRD profile fitting revealed that the sample contains mainly Silicon oxides (of two forms) and the organic compound contains As which can detected by XRF and iTRAX, However both iTRAX and WD -XRD are not capable of showing elements with atomic number less than 11 such as carbon, nitrogen, oxygen, and hydrogen etc. Loss on Ignition (L.O.I) values obtained during XRF experiments (see Table 4) indicates the possibility of organic contents in the samples studied, and this is supported by XRD results showing $As_6C_{36}O_{36}H_{54}$ for sample H2 (see Table 3 and Figure 4). Analysis of our quartz sinter sample from Steamboat Spring (H2) revealed the majority of the quartz is hexagonal but some quartz crystals are orthorhombic. This is unusual as hexagonal quartz crystals usually form under higher pressure and sinters from at the surface, under low pressure. Our quartz sample was removed from a surface outcrop with no evidence of burial. For hexagonal quartz crystals to form, they require high pressure which forces the atoms to occupy a smaller volume, resulting in more closepacked arrangements and lower symmetric crystal structures (Prewitt *et al*. High Pressure Mineralogy: Chapter 9).

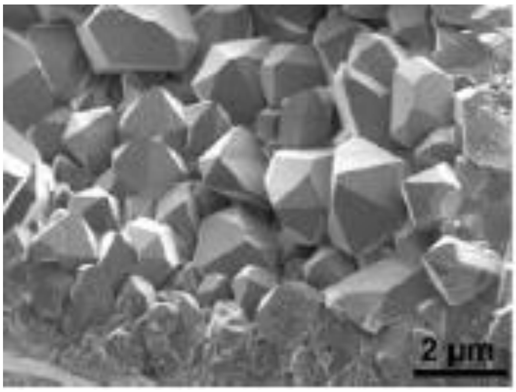

Figure 5: Scanning Electron Microscope image of Steamboat Spring quartz sinter (Lynne et al., 2007).

Scanning Electron Microscopy observations of the quartz sinter from Steamboat Springs (Fig. 5) does reveal closely-packed, doubly-terminated quartz crystals have formed in this low pressure setting.

5. CONCLUSION

The combination of XRD, XRF and iTRAX X-ray methods is useful in tracking changes in fluid chemistry over time. While iTRAX results provided in-situ elemental distributions for the scanned area/surface of each sample, WD-XRF provided more accurate elemental bulk composition for each sinter sample. Using elemental information as references for HighScore Plus analysis on XRD data, it was possible to acquire the correct mineralogy for crystalline samples. These high-resolution techniques have characterised compositional differences recorded from discharging alkali chloride hot springs which has been preserved in the sinters from two different USA geothermal fields. Our study highlights changes in fluid chemistry not only between the two geothermal systems, but even within the same system over different time periods.

REFERENCES

Anders Liljas, Acta Crystallographica. (2013). A69, pp10–15

Rasel Ds, Md. Eaqub Ali, Sharifa Bee AbdHamid, Current Application of X-ray Powder Diffraction –A review, Reviews on Advanced Materials Science. 38(2014); p.96-109

Croudace, I.W., Rindby, A., Rothwell, R.G., 2006. ITRAX: description and evaluation of a new multi-function X-ray core scanner. In: Rothwell, R.G. (Ed.), New Techniques in Sediment Core Analysis. Geological Society, London, Geological Society Special Publication, 267, p. 51–63

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. Sedimentary Geology 179, p.249-278.

Lynne, B.Y. Campbell, K.A., Moore, J.N., Browne, P.R.L. 2008. Origin and evolution of the Steamboat Springs siliceous sinter deposit, Nevada, USA. Sedimentary Geology 210, p.111-131.

Charles T. Prewitt, Robert T. Downs, Ultra High-pressure Mineralogy, Chapter 9 High Pressure Crystal Chemistry

Herdianita, N.R., Browne, P.R.L., Rodgers, K.A., Campbell, K.A., 2000. Mineralogical and textural changes accompanying ageing of silica sinter. Mineralium Deposita 35, p.48–62.

Fournier, R.O., Rowe, J.J., 1966. Estimation of underground temperatures from the silica content of water from hot springs and steam wells. American Journal of Science 264, p.685– 697.

Lynne, B.Y. Campbell, K.A., James, B.J., Browne, P.R.L., Moore, J.N. 2007. Tracking crystallinity in siliceous hot-spring deposits. American Journal of Science, vol. 307, p. 612-641.