Revision 1

Multinuclear NMR study of Cs-bearing Geyserites of the Targejia Hot Spring Cesium Deposit in Tibet

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ABSTRACT

The large scale Targejia hot spring type Cs deposit in Tibet is unique and still active today with the distribution of hot springs being controlled by tectonic movements of the Tibetan Plateau. The ore bodies of the Targejia Cs deposit are mainly composed of geyserite, a Cs-containing opal. In this study, a combination of X-ray diffraction, infrared spectroscopy and $^{29}$Si, $^1$H, $^{133}$Cs magic-angle spinning nuclear magnetic resonance (MAS NMR) were used to study the location and mobilization of Cs in geyserites. $^{29}$Si NMR spectra indicate the relative amounts of $Q^2$, $Q^3$ and $Q^4$ species vary in geyserite samples of different mineralization stages. Based on the $^{133}$Cs chemical shift as well as the change in $^{29}$Si chemical shift ranges (especially for $Q^2$), cesium is inferred to associate with $Q^3$ and $Q^2$ silanol groups, where it is coordinated by $O^-$, $OH^-$ and $H_2O$ as a network modifying cation. As Cs-bearing geyserite ages and dehydrates, $Q^2$ and $Q^3$ polymerize giving an increase in $Q^4$. This is accompanied with a decrease in Cs content indicating that Cs may be leached out from the opals as it loses its original coordination environment in the silicate framework.
Introduction

The east-west-trending Himalayan Geothermal Zone in the Tibet Plateau is one of the most active geothermal areas on earth. It is distributed along the Yanglu Zangbo “suture line” between the Eurasian Plate to the north and the India Plate to the south, and is controlled by the subduction of the Indian Plate underneath the Tibetan Plateau. Geothermal activities in the Tibetan Plateau are typically in the form of hot springs, with varieties such as Si-, Ca-, S- and salt-rich geysers (Zheng 1995; Li et al. 2006). These hot springs are important not only for the study of the plateau evolution but also for the industrial utilization of geothermal energy and epithermal mineral deposits. Geothermal solutions from these hot springs are important sources for rare-metal mineralization in numerous saline lakes in Tibet (Zheng 1995). These hot springs and associated geothermal activities in the Tibet Plateau provide a unique natural laboratory for investigating modern epithermal mineralization and other ongoing ore-forming processes.

Cesium is an alkali metal that has been utilized widely in high-technology and military industries due to its excellent photon-electronic and chemical properties (Zheng 1995; Zhao et al. 2006, 2008). The unique hot spring Cs deposits in Tibet have a close genetic relationship with high-temperature geothermal anomalies, i.e., above 60 °C and with pH values of 8.5 to 9.0 (Shen et al. 2011). Due to the effects of the post Tibetan Plateau Collision, the geochemistry of these deposits is characterized by enrichments in B, Cs, Rb and Li (Zheng 1995; Zhao et al. 2006, 2008). Using electronic spin resonance (ESR) and other geochronological methods, the mineralization of Cs-bearing geyserite deposits at the Gulu and Targejia areas has been determined to have commenced around 0.5 Ma and remains

The mineral assemblages of the Cs-bearing geyserite deposits at the Gulu and Targejia areas are dominated by opals, which were precipitated from silica-rich solutions (Zheng 1995; Shen et al. 2011). Opals are hydrous minerals consisting of 150 to 300 nm diameter spheres of silica, which exhibit various degrees of structural disorder (Brown et al. 2003). Stages of opal solid-state transformations are commonly designated as opal-A (amorphous), opal-C (cristobalite) and opal-CT (cristobalite-tridymite), with the final stage being indicated by the presence of quartz (de Jong et al. 1987; Graetsch et al. 1994; Brown et al. 2003). Water is incorporated into the opal structure as molecular water (H\textsubscript{2}O) and silanol (Si-OH) groups. Both vicinal (SiO\textsubscript{3}(OH), Q\textsuperscript{3}) and geminal (SiO\textsubscript{2}(OH)\textsubscript{2}, Q\textsuperscript{2}) hydroxyl groups are likely to occur at structural defects caused by incomplete polymerization of the silica tetrahedra, or at the surfaces of the silica spheres where the continuous silica network is interrupted (Paris et al. 2007). The solid-state transition between amorphous and crystalline opal should show up as variations in the local Si environments, which can be characterized by \textsuperscript{29}Si nuclear magnetic resonance (NMR) spectroscopy, while the speciation and dynamic behavior of hydrogen in opals may be probed by \textsuperscript{1}H NMR (Brown et al. 2003).

Here we combine X-ray diffraction (XRD), infra-red (IR) spectroscopy and magic-angle spinning (MAS) NMR spectroscopy to examine the structural sites occupied by Si, H and Cs in Cs-geyserites from the Targejia deposit. These data allow us to probe the local structure and connectivity among Si, H and Cs atoms. The atomic environment and migration behavior of Cs in Cs-geyserites will be discussed in this paper. The term “Cs-geyserite” will be used for the opal mineral assemblages of the Cs-bearing geyserite deposits at the Targejia area.
throughout this paper.

**The Targejia Hot Spring Cesium Deposit**

The largest hot spring type cesium deposit at the Targejia area is located in Ang Ren County of Tibet at an elevation of 5,000 m. Zheng (1995) reported a total reserve of ~1.446 x 10^4 T Cs with an ore grade up to 9.8 x 10^{-3} wt. %. Outcrops of Cs-geyserites at the Targejia deposit are in the forms of blocks (30 x 20 x 7 m^3), cones (radius 0.2-0.5 m; height 0.5-0.8 m), and veins (5-10 m long; 0.2-3 m wide). Individual ore-bodies are distributed at the surfaces along the fractures of Gangdise glacial moraine, or are situated on terraces and in river beds of the Changmaqu River. Mineralization at the Targejia Cs deposit has been classified into five stages from the top to the bottom of the terraces which have been dated by ESR and other methods (Zhao et al. 2006). The periods for the five stages of mineralization correspond to 255-201 ka, 99 ka, 39.4-25.0 ka, 14.8-4.4 ka, and recent.

Cs-geyserites are composed of amorphous hydrous silica, which is mostly in a form of opal-CT for the early mineralization stages and opal-A for late stages. Granular opals exist through all stages, whereas coliform opals occur mainly in the late stages. Cauliflower-like, mega-grained massive and corrosion textures caused by dehydration processes are often observed in the early stages whereas fine-grained massive and porous textures are found only in the late stages. Other textural varieties such as clastic, stratiform, densely massive, stalactitic, colloidal, brecciated or conchoidal are also present (Zhao et al. 2006).

Geochemical analyses by Zheng (1995) showed that the Cs concentration at the Targejia deposit has an inverse correlation with the SiO_2 content and varies systematically with the age of mineralization. These relationships have been partly attributed to changes in the Cs and
SiO$_2$ concentrations in the hot springs with time. Another contributing factor is the increase in the structural order of opals due to the progressive dehydration and polymerization of geyserites from the early to late mineralization stages (Zheng 1995; Zhao et al. 2006, 2008).

**Materials and Methods**

**Sample preparation**

Representative samples of Cs-geyserites from each of the five mineralization stages at the Targejia deposit were supplied by Dr. Yuanyi Zhao and Prof. Mianping Zhang. Samples 8-3-10-2, 8-3-10-3 are from initial stage of mineralization; 8-3-8-1, 8-3-5-1 and 8-3-5-2 belong to the second stage; third stage samples include 8-3-4-1, 8-3-4-2, 8-2-4-2 and 8-3-3-1; 8-3-1-1 and 8-3-1-3 are from the fourth stage; fifth stage mineralization samples are 8-3-2-7, 8-3-2-18, 8-3-2-26 and 8-3-2-30. Samples were various shades of gray, tan, light grayish-green or pink. The chemical compositions of the Cs-geyserite samples, which have been previously analyzed by energy spectra (Zhao et al. 2008), contain 90-98 wt. % SiO$_2$ and 0.6-2.6 wt. % Cs$_2$O (Table 1).

Opals from these samples were handpicked under a binocular microscope and then ground to fine powders using an agate mortar and pestle for XRD, IR and MAS NMR spectroscopy. Samples with high Cs content are chosen for $^{133}$Cs MAS NMR experiments.

In order to investigate the structural changes as opal ages, a geyserite sample was subjected to high energy ultrasonic vibration in an attempt to speed up the polymerization processes. A portion of 3rd stage Cs-geyserite sample 8-3-4-2 (0.3 g) was immersed in 4 mL of NaHCO$_3$ solution (pH = 8.5), then stirred by high energy ultrasonic vibration (KQ-100DB NC Ultrasonic Cleaner) for six hours, and finally dried in an oven at 80 °C for a further six hours.
before NMR analysis.

**X-ray diffraction**

Powder XRD data were collected at room temperature with a computer-controlled Bruker D8 Advance Diffractometer (Chinese Academy of Geological Sciences) using Cu $K_{\alpha}$ radiation in a step width of 0.02° for $\Delta 2\theta$ and a $2\theta$ range from 10 to 70°, with scanning speed of 3°/min and count time of 5 s per step.

**IR spectroscopy**

Hand-picked opals were ground to a fine powder and combined with KBr (99.9%) and pressed into pellets. IR absorption spectra were recorded at room temperature on a Perkin-Elmer 580 double-beam IR spectrometer with a wave number range from 400 cm $^{-1}$ to 4000 cm$^{-1}$, and a 4 cm$^{-1}$ resolution (Chinese Academy of Geological Sciences, and Shanghai Key Laboratory of Magnetic Resonance).

**MAS NMR Spectroscopy**

$^{29}$Si MAS NMR experiments were measured on Bruker DSX-300 spectrometer ($B_o = 7.05$ T) using a 7 mm Bruker MAS probe (Shanghai Key Laboratory of Magnetic Resonance). Samples were packed within ZrO$_2$ rotors (7.0 mm outer diameter (o.d.)) and spun to 3,000 Hz. Decoupled Bloch $^{29}$Si MAS NMR spectra were acquired with a recycle delay time of 120 s and $^1$H decoupling with a $\nu_{ef}$ of 50 kHz was applied during the acquisition. The $^1$H-$^{29}$Si cross polarization (CP) MAS NMR spectra were acquired using a contact time of 2 ms. The Bloch decay and CP experiments were acquired using between 200 and 2,048 co-added transients.

$^{29}$Si MAS NMR experiments were also acquired using a Bruker Avance III 500 ($B_o = 11.74$ T) spectrometer with a triple-resonance Bruker broadband probe (Department of
Chemistry, University of Manitoba). Samples were packed in 3.2 mm ZrO$_2$ rotors (22 μL sample volume) and a spinning frequency between 4,200 and 8,000 Hz used. $^{29}$Si spectra were acquired using both Bloch decay (average recycle delay of 60 s) and CP experiments (with a recycle delay of 2 s, and contact time of 2 ms), and between 13,000 and 20,000 co-added transients. The geyserite sample recorded were a faint pink/purple in color suggesting trace amounts of paramagnetic impurities, likely Mn. The recycle delays for CP experiments were determined from $^1$H spin-lattice experiments, while $^{29}$Si Bloch experiments were recorded at 30, 60, 120 and 300 seconds using a tip angle of 30°. $^{29}$Si NMR spectra were referenced to 6.68 ppm using hexamethylsiloxane as a secondary external reference relative to TMS (0.0 ppm).

$^1$H Bloch decay and DQ-filtered MAS NMR spectra were also acquired on a Bruker DSX-600 spectrometer ($B_0=14.1$ T) using a 2.5 mm Bruker MAS probe (Shanghai Key Laboratory of Magnetic Resonance). The Bloch decay $^1$H MAS NMR spectra were acquired with a recycle delay time of 4 s and a spinning frequency of 25,000 Hz. The DQ-SQ sequence was used for the $^1$H DQ-filtered NMR experiments (Schnell and Spiess 2001) with 80 μs for both the excitation and reconversion time, and MAS spinning frequencies were 25,000 Hz with a ν$_{rf}$ of 37 kHz. Chemical shifts for $^1$H was referenced to tetramethylsiliane (TMS) to 0.00 ppm.

$^{133}$Cs MAS NMR spectra were acquired using a Varian UNITY $^{133}$Inova 600 ($B_0=14.1$ T) spectrometer with a 5 mm double resonance Varian-Chemagnetics probe (H/F-X) (Department of Chemistry, University of Manitoba). A hand-picked opal sample was ground to a fine powder and packed into a 5 mm outer diameter Si$_3$N$_4$ rotor (140 μL sample volume).
Bloch decay (40° tip-angle) and Hahn-echo ($\pi/2-\tau-\pi, \pi = 8 \mu$s) spectra were acquired using 50,000 co-added transients, 5 s recycle delays and a spinning frequency of 10,500 Hz. Spectra were referenced to 0.5 M CsCl (0.00 ppm). In previous studies (Kroeker et al. 2010), crystalline synthetic cesium-containing oxides were determined to show long spin-lattice relaxation times (e.g., 100s of seconds), therefore, caution was taken when studying Cs-containing oxides. In this study, the absence of highly crystalline Cs sites was checked using recycle delays of 8 minutes over a period of 3 to 4 days. Again, a small fraction of paramagnetic transition metals assisted in shortening the relaxation times (spin-lattice), enabling short recycle delays.

**Results and Discussion**

*Characterization of the samples by XRD and IR*

All of the samples were analyzed by XRD and IR. Representative XRD results (Fig. 1) show that the samples from the first two stages (8-3-10-3, 8-3-8-1) are characterized by a higher degree of crystallization indicated by quartz peaks whereas the last stage sample is an amorphous SiO$_2$ phase (opal) (8-3-2-18). The XRD pattern of 8-3-4-1 indicates that the third stage is mainly composed of opal-A with minor quartz. Minor amounts of clastic plagioclase, orthoclase as well as quartz were found within the fourth stage Cs-geyserite sample (8-3-1-1). Overall the XRD patterns (Fig. 1) show a general trend from early to late stages, with decreases in the degree of crystallization and increases in opal-A.

In the IR spectra, the bending vibration absorbance bands at 798 cm$^{-1}$, 694 cm$^{-1}$ and 472 cm$^{-1}$, which are typical of opals (Zheng 1995), are present in the samples 8-3-10-2 (1$^{st}$ stage), 8-3-8-1 (2$^{nd}$ stage) and 8-3-2-18 (5$^{th}$ stage) (Figs. 2a and 2b). These bands can be assigned to
tetrahedrally coordinated silicon (Graetsch et al. 1994) together with the intense band at approximately 1100 cm\(^{-1}\) present in the IR spectra for all the samples (Fig. 2a). The absorbance band near 620 cm\(^{-1}\), which is characteristic of low-cristobalite (Etchepare et al. 1978; Graetsch et al. 1994), is absent in these IR spectra (Figs. 2a and 2b) indicating that the Cs-geyserite samples in this study are mainly opal-CT and opal-A. The IR spectra of opal-CT and opal-A differ only in the width and line-shape of the absorption bands (Fig. 2a) with an increase in the bandwidth at the region 3500 cm\(^{-1}\) and for the peaks at smaller wavenumbers occurring in the order opal-C, opal–CT and opal-A.

In summary, the XRD and IR data show that the minerals of the Targejia Cs deposit in Tibet are mainly composed of opal-A and opal-CT with small amounts of quartz present in samples 8-3-10-2 (1\(^{st}\) stage), 8-3-3-1 and 8-3-1-1 (both 4\(^{th}\) stage), with minor plagioclase and orthoclase also detected in the latter two samples.

**MAS NMR Spectroscopy and structural implications**

Bloch decay \(^{29}\)Si MAS NMR spectra at both 7.05 T and 11.74 T show a main resonance centered at -111 ppm, with a full width at half maximum (FWHM) of \(~9.5\) ppm (Fig. 3a) and a shoulder on the left-hand side (i.e., to higher frequency). The resonance at -111 ppm is characteristic of Q\(^4\) structural arrangements (all bridging oxygens) in amorphous silica (Engelhardt and Michel 1987; de Jong et al. 1987). This chemical shift is between the experimental chemical shifts for cristobalite and tridymite (de Jong et al. 1987). According to Chemtob et al. (2012), too short of a recycle delay time may result in significant underestimation of Q\(^4\) but the delay times of 60 and 120s used for these experiments are believed to be sufficient to eliminate this problem. The asymmetrical shoulder observed on
the left-hand side can be explained by the additional overlapping resonances from silanol
groups, Q\(^3\) (SiO\(_3\)(OH)) and Q\(^2\) (SiO\(_2\)(OH)\(_2\)). The width of the \(^{29}\text{Si}\) MAS NMR resonances in
the Cs-geyserites is caused by a distribution of silica species that vary in both bond distances
and Si-O-Si angles. Such distribution represents a significant extent of relative local disorder
(de Jong et al. 1987; Brown et al. 2003). The empirical equation \(\delta_{\text{iso}} = -19.8215 - 0.608526 <\theta>\)
can be used to correlate \(^{29}\text{Si}\) chemical shift (ppm) with average <Si-O-Si> angle (<\theta>)
(Thomas et al. 1983). This equation gives <\theta> for Q\(^4\) of 151.5°, which is between the values
of 151° for opal-A and 152° for opal-CT previously determined by de Jong et al. (1987).

\(^1\text{H}-^{29}\text{Si}\) CP MAS NMR spectroscopy resolves the higher frequency shoulder into multiple
resonances around -101 ppm and -90 ppm (Figs. 3b and 4). The intensity of the main
resonance (-111 ppm) detected by the Bloch decay experiment decreases relative to the newly
resolved resonances for the Cs-geyserites of all mineralization stages (Fig. 3b and 4). The
relative intensity for Q\(^4\) units suffers in CPMAS spectra because the longer distances to -OH
result in poor \(^1\text{H}\) spin-transfer to \(^{29}\text{Si}\), in contrast to the proximity of the hydroxyl (OH)
groups in Q\(^3\) and Q\(^2\) silanol groups, which enable more efficient magnetization transfer. The
resonance at -101 ppm is assigned to Q\(^3\) vicinal silanol groups, and the resonance ~ -90 ppm
to Q\(^2\) geminal silanol groups. For Q\(^4\) and Q\(^3\) species, both isotropic chemical shifts and
FWHM of 9.5 ppm agree well with published results for opals (Brown et al. 2003).

The presence of Q\(^2\) and Q\(^3\) silanol groups with protons attached to the non-bridging
oxygen agrees with research showing that most of the water present within the Cs-geyserites
is chemisorbed (Graetsch et al. 1994; Paris et al. 2007).

The line-shapes of \(^1\text{H}-^{29}\text{Si}\) CPMAS spectra for the geyserite samples at each
mineralization stage are similar; however, there are variations of the relative intensity ratios for the Q$_2$, Q$_3$ and Q$_4$ environments for different samples, and for different slices through the same sample, indicating the evolution of geyserites. For example, the relative intensity for the Q$_4$ resonance located in the lower section of Sample 8-3-4-2 (3rd stage) is lower than that for the upper and middle sections of the same sample (Fig. 4).

$^1$H DQ-filtered experiments are often used to detect $^1$H resonances from strong correlated $^1$H-$^1$H dipolar interactions (i.e., hydrogen bonding), whereas the Bloch experiment excites all the $^1$H environments equally within a sample (Schnell 2004; Paris et al. 2007). The $^1$H MAS NMR spectrum of Sample 8-3-2-30 (5th stage) exhibits three resonances: an intense narrow resonance around 4 ppm with a FWHM of 2-3 ppm, a broad shoulder between 6.5 and 8 ppm and a narrow, less intense resonance at 0.9 ppm (Figs. 5a and 5b). $^1$H resonances located below 1.8 ppm usually are assigned to internal isolated silanols with very weak or no hydrogen-bonding (Hansen et al. 2008, 2009; Paris et al. 2007). Therefore, the resonance located at 0.9 ppm is assigned to weakly hydrogen-bonded or to isolated hydroxyls associated with Q$_2$/Q$_3$ environments. The dominant peak at ~4 ppm is assigned to water within geyserite (Paris et al. 2007). $^1$H NMR peaks above 7 ppm correspond to the protons strongly bonded to the non-bridging oxygen atoms (Hansen et al. 2008, 2009; Xue and Kanzaki 2009), therefore, the broad shoulder between 6.5 and 8 ppm may result from strong hydrogen-bonded hydroxyls, internal Q$_2$ and Q$_3$ silanols, residual physisorbed water molecules, or Cs environments such as Si-OH---Cs. These assignments are consistent with those in opals by Paris et al. (2007). $^1$H spins in geyserite are present either in the form of “free” water which is not in a correlated dipolar state due to the mobility, or hydrogen-bonded where the $^1$H spins
are strongly correlated. The relative intensities of $^1$H DQ-filtered spectrum are scaled by the
magnitude of the homonuclear dipole–dipole couplings that the respective $^1$H spin
experiences (Schnell et al. 2001; Paris et al. 2007).

The assignments of $^1$H NMR peaks were verified by the DQ-filtering effect, as this
causes intensity from the mobile water resonance to decrease, while signals from stronger
hydrogen-bonded hydroxyls and internal Q$^2$ and Q$^3$ silanols are enhanced (Fig. 5c). The cross
peak in DQ-filtered 2D $^1$H NMR spectrum of the 5th stage Sample 8-3-2-30 (Fig. 5d) indicates
a correlation between water (4.6 ppm) and the stronger hydrogen-bonded hydroxyls (above
6.5 ppm). Therefore, some water within geyserites is near OH groups, interacting with these
groups through hydrogen bonding. The peak at 4.6 ppm of the DQ spectrum becomes broader
than the corresponding peak of MAS NMR due to the signals from both mobile as well as less
mobile water (Fig. 5).

Cesium-133 (I=7/2) is a useful nucleus for NMR study due to its 100% natural abundance,
and a moderate gyromagnetic ratio ($\gamma$) (Kim et al. 1996a, 1996b; Weiss et al. 1990a, 1990b;
Ejeckam and Sherriff 2005). Because of the small quadrupolar moment of $^{133}$Cs and the high
magnetic field (14.1 T) used here, $^{133}$Cs resonances do not show the characteristic
singularities of second-order broadening of the central transition. As the second-order
quadrupolar interaction induces a shift of less than 11 Hz for $^{133}$Cs, the center-of-gravity of
the resonance can be taken as an isotropic chemical shift (Michaelis et al. 2007, 2009;
Kroeker et al. 2003, 2006). The large number of electrons causes Cs nucleus to be very
polarizable with a wide chemical shift range of 350 ppm (Mason 1987; Michaelis et al. 2007;
Michaelis and Kroeker 2009; Weiss et al. 1990a, 1990b) and hence sensitive to small changes
The $^{133}$Cs MAS NMR spectra of Cs geyserites have a single broad Gaussian shaped resonance centered at ~ -40 ppm with a FWHM of 9 ppm (Fig. 6). The lack of additional narrow resonances in $^{133}$Cs MAS NMR spectrum due to crystalline Cs, together with optical microscopic observations, and IR and XRD analyses indicates that there are no independent Cs minerals in these samples (Kroeker et al 2010, Greer and Kroeker 2012). The $^{133}$Cs chemical shift of ~-40 ppm precludes the hydration of Cs in Cs-geyserites because $^{133}$Cs chemical shift for Cs species in solution ranges from 0 to 69 ppm (Mason 1987; Weiss et al. 1990a, 1990b).

The negligible content of trivalent cations such as Al in Cs-geyserite precludes Cs from being a charge balancing cation. Unlike strongly hydrated cations such as Li, Ca and Mg, weakly hydrated cations such as K and Cs are expected to come into direct contact with the defects (surfaces) within the opal structure (Kim et al. 1996a, 1996b; Weiss et al. 1990a, 1990b). Therefore, the $^{133}$Cs chemical shift observed for Cs-geyserites is neither caused by separate Cs minerals nor by Cs surrounded by a complete hydration shell. It is likely to arise from Cs in structural environments similar to the Stern Layer in clay minerals, where Cs is located at Q$^2$ and Q$^3$ sites caused by structural defects or surfaces (Weiss et al. 1990a, 1990b; Kim et al. 1996a, 1996b; Ejeckam and Sherriff 2005).

Cesium in such environments is tightly bound to and coordinated by O atoms of the Si tetrahedra, and may also be surrounded by some water molecules which interact with stronger hydrogen-bonded hydroxyls or internal silanol groups as shown by $^1$H NMR spectra. As a result, the chemical shifts around -90 ppm for Q$^2$ in Cs-geyserite samples would be shifted...
toward to higher field compared with those for the Q$^2$ environments without adjacent Cs.

Due to the size of the Cs cation, the coordination environment can vary significantly and may be probed via NMR. $^{133}$Cs, $^{67}$Li, $^{23}$Na, $^{27}$Al and $^{29}$Si resonances have been shown to shift to lower frequency (i.e., more shielded) with an increase in coordination number for ionic solids (Smith and Blackwell 1983; Xu and Stebbins 1995; Michaelis et al. 2007). Weiss et al. (1990a) assigned a $^{133}$Cs peak at ~56 ppm to hydrated Cs sites with a coordination number of 9. The resonance centered at -40 ppm in Fig. 6 is probably from the 10- to 12-fold Cs polyhedron mainly coordinated by OH and basal O atoms of the SiO$_4$ tetrahedron.

Thermodynamic calculations show that the hydrated silica series composed of Si(OH)$_4$ tetrahedra have much weaker bonding between Si and OH than for Si-O (Zheng 1995). Based on the principles of hydrothermal mineralization and colloid chemistry, Zheng (1995) asserted that strong electrolyte alkaline elements such as Cs can accelerate the precipitation of colloidal hydrous SiO$_2$ and form opals. Such a precipitation process leads to the incomplete poly-condensation of silica tetrahedra and forms silica spheres. The surfaces of silica spheres can also interrupt the continuous silica network. This can result in the formation of both vicinal and geminal hydroxyl groups. The hydroxyl groups terminating Si tetrahedra in Cs-geyserite cause local negative charges at the internal structural defects or near the surface of silica spheres in Cs-geyserites, which are not fully balanced by Si$^{4+}$. Cs$^+$ is then attracted electrostatically by the negative charges resulting in Cs adsorption at defect or surface of Q$^2$, Q$^3$ sites (silanol groups), therefore, Cs is most likely located at Q$^2$, Q$^3$ sites in geyserites, and connected tightly with the Si network of opals.

As the opals age, the SiO$_4$ tetrahedra coalesce and polymerize, then opal-A evolves to
opal-CT or quartz, so the structure becomes more ordered and will eventually crystallize. Such structural reorganization results in the loss of ‘bound’ water and silanol groups (Paris et al. 2007). Sample 8-3-4-2 (3rd stage) was used in an attempt to accelerate such a polymerization process by subjecting the sample to high energy ultrasonic vibration before running a second $^1$H-$^{29}$Si CP MAS NMR spectrum. The intensity for the Q$^4$ peak in the 3rd stage Sample 8-3-4-2 (Fig. 7) is shown to increase after this ultrasonic vibration process. This change possibly results from the reaction of Si-OH + HO-Si $\leftrightarrow$ Si-O-Si + H$_2$O. As a result of such a solid-state transition in Cs-geyserite, Cs may lose its coordination environments and be leached out during the progressive polymerization process as opals age.

In summary, $^{29}$Si MAS and $^1$H-$^{29}$Si CP MAS spectra reveal the main structural unit in Cs-geyserites is Q$^4$ silicon tetrahedra, with limited amounts of Q$^3$ and Q$^2$ species. Characterization of the hydroxyl groups was achieved using NMR chemical shift information, $^1$H-$^{29}$Si CPMAS and DQ-filtered $^1$H spectra. $^{133}$Cs MAS NMR spectroscopy suggests that Cs in Cs-geyserites is associated with silanol groups and is coordinated mainly by OH and basal O atoms of silicate tetrahedra, rather than being in separated phases such as crystalline Cs oxides or fully hydrated Cs coordination. $^1$H-$^{29}$Si CP MAS NMR spectra before and after ultrasonification indicate the process of SiO$_4$ coalescence and polymerization in Cs-geyserites. Leaching of Cs during such a process, may be the reason for Cs concentration decreasing with aging.

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Figure 1. XRD patterns for the representative samples of the five mineralization stages (a: stage 1 (Sample 8-3-10-3); b: stage 2 (Sample 8-3-8-1); c: stage 3 (Sample 8-3-4-1); d: stage 4 (Sample 8-3-1-1); e: stage 5 (Sample 8-3-2-18)). A-op: A-opal; CT-op: CT-opal; Qtz: quartz; Pl-Or: Plagioclase-Orthoclase.
Figure 2. Infrared absorption spectra of (a) Cs-geyserite opal-CT (1st stage Sample 8-3-10-2) and opal-A (5th stage Sample 8-3-2-18) and (b) an enhanced region (1000 cm⁻¹ to 400 cm⁻¹) of 2nd stage Sample 8-3-8-1.

Figure 3. $^{29}$Si MAS (a) and $^1$H-$^{29}$Si CPMAS (b) NMR spectra for 3rd stage Sample 8-3-1-1 at 11.74 T (vertical lines for guiding eyes)
Figure 4. $^1$H-$^{29}$Si CP MAS NMR spectra of Cs-geyserite sample 8-3-4-2 of 3rd stage at 7.05 T (dash lines for guiding eyes). The three spectra represent different subsections from the sample: (a) top subsection, (b) middle subsection and (c) lower subsection.

Figure 5. $^1$H MAS NMR of Sample 8-3-2-30 of 5th stage using a Bloch decay (a), enhanced isotropic region (b) and a 1D slice of the DQ-filtered spectrum (c), and two-dimensional DQ-filtered spectrum acquired at 14.1 T (d), exhibiting a correlation between H$_2$O and OH$^-$ groups (shown by the cross section).
Figure 6. $^{133}$Cs MAS NMR spectrum of Cs-Geyserite (Sample 8-3-1-1 of 3$^{rd}$ stage) at 14.1 T. Spinning side bands flanking the central transition (0 to -100 ppm) are present on either side.

Figure 7. $^1$H-$^{29}$Si CPMAS spectra for Sample 8-3-4-2 of 3$^{rd}$ stage at 7.05 T before (a) and after (b) stirring by the high-power ultrasonic vibration.
Table 1: The chemical compositions of the geyserite specimens (Zhao et al. 2006)

<table>
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<th>Sample number</th>
<th>8-3-10-2</th>
<th>8-3-5-2</th>
<th>8-3-4-2</th>
<th>8-3-1-3</th>
<th>8-3-2-30</th>
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<tr>
<td>Mineralization stage</td>
<td>1st stage</td>
<td>2nd stage</td>
<td>3rd stage</td>
<td>4th stage</td>
<td>5th stage</td>
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<td>Na$_2$O</td>
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<tr>
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<td>$\Sigma$ (Na$_2$O+Al$_2$O$_3$+K$_2$O+CaO)</td>
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<td>1.82</td>
<td>4.66</td>
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