Characterisation and genesis of the chalcedony occurring within the Deccan lava flows of the LIT hill, Nagpur, India

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The Deccan trap basaltic lava flows host a plethora of secondary minerals, notably zeolites, quartz and calcite. These minerals occupy the vesicles and cavities that are formed during the solidification of the lava flows. Much attention has been given to beautifully developed zeolites of the Deccan traps and well-crystallised quartz varieties such as rosy quartz and amethyst. However, a group of minerals consisting of cryptocrystalline and amorphous silica did not receive much attention despite their consistent occurrence in all parts of the Deccan large igneous province. The freshly exposed samples of the chalcedonic silica occurring in the vesicular basalt at the Laxminarayan Institute of Technology (LIT) hill, Nagpur University Campus, were studied, one of which was studied in detail using X-ray diffraction analysis, differential thermal analysis, thermogravimetric analysis, Fourier transform infrared and scanning electron microscope–energy dispersive spectroscopy. The present study has demonstrated that the secondary silica occupying vesicles in the basaltic lava flows was length-fast chalcedony showing fibrous morphology overprinted by grainy morphology. It was concluded that the mother fluid was a hot ($\sim 100\text{--}300^\circ\text{C}$) aqueous solution, which was acidic in nature and high in sulphur, probably derived from the host Deccan trap basaltic magma itself.

Keywords. Chalcedony; Deccan traps; basalt; secondary silica; amygdules.

1. Introduction

Amygdules (also known as amygdaloids) are gas cavities, or vesicles, in igneous rocks (usually volcanic or shallow intrusive) that are filled, or partially filled, with secondary minerals (Rakovan 2005). These minerals may have a late-stage magmatic origin or, more commonly, may form from post-magmatic aqueous solutions (Chemtomb and Rossman 2014). Common minerals in amygdules

include calcite, quartz, chalcedony, chlorite and zeolites. The Deccan trap basalts are bestowed with a rich bounty of secondary minerals (e.g., Ottens 2003).

These deposits are formed from hydrothermal solutions that permeated basaltic lava flows and deposited copper-rich and other minerals by open-space filling (i.e., fractures and vesicles) and replacement. Vesicles are created by the expansion of gas bubbles or steam within molten lava. They

are, therefore, usually rounded, elongated or almond-shaped. Vesicles and hence amygdules are generally more pronounced in basalts than in other volcanic rock types. This is partly because of the lower viscosity of basaltic lavas, which allows gas bubbles to readily expand before the lava solidifies. Vesicles are typically an inch or two in maximum dimension; however, they can be much larger. The larger ones are commonly known as pockets or vugs and are less likely to become completely filled by secondary minerals. If mineralised, they usually exhibit varying degrees of lining. The spectacular museum specimens of zeolites from the Deccan traps in India (Ottens 2003) are found mostly as amygdules or pocket linings. In some lava, rising gas bubbles may stretch out to form tubular vesicles. Mineralisation of these vesicles forms tube or pipe amygdules. Large tubular gas pockets (often many feet long) lined with amethyst and other accessory minerals, colloquially known as ‘cathedrals’, are common in the basalts of Rio Grande do Sul, Brazil (Rakovan 2005). The term ‘amygdule’ is derived from the Greek word for ‘almond’. There are some ambiguities in the semantics given above. Specifically, the dividing line between an amygdule and a mineralised pocket, and the degree of vesicle infilling necessary to be called an amygdule, is not precisely defined – although, vesicles and hence amygdules are usually less than 2 inches in size.

The Deccan large igneous province (LIP) is known for the occurrence of secondary minerals, such as zeolites, phyllosilicates, hydrated sulphates, carbonates, tungstates–molybdates, and even native elements like copper in cavities of varying shapes and sizes (Sukheswala and Poldervaart 1958; Sukheswala *et al.* 1974; Avasia and Gangopadhyaya 1984; Jeffery *et al.* 1988; Apte and Phadke 1996; Ottens 2003). Their presence is particularly conspicuous in ‘pahoehoe’ (i.e., compound) type lavas than ‘aa’ (i.e., simple) type lavas (Phadke and Bapat 1984). Zeolites (Apte and Phadke 1996 and references therein) and other aesthetically important minerals such as amethyst and calcite (Patil *et al.* 1981; Ottens 2003) were the subject of most of the previous studies on the secondary minerals of the Deccan traps. Although there are some passing references to the occurrence of cryptocrystalline and amorphous silica (e.g., Parthasarathy 2006), the hydrous (cryptocrystalline and amorphous) silica did not receive any significant attention despite their perpetual occurrence all over the mineralised areas.

The cryptocrystalline and amorphous silica, which commonly occur in the form of chalcedony, opal, wood-opal, onyx and other forms are omnipresent within the Deccan traps basaltic terrain. It is known that natural chalcedony forms under near surface conditions at low temperatures. These conditions are restricted to sedimentary and low-temperature hydrothermal environments. The widespread association of chalcedony with opal and similar material and the conversion of opal to chalcedony are among the most-studied phenomena (Barth 1952; Williams *et al.* 1954; White 1955; Pettijohn 1957; Pittman 1959). Chalcedony has certain distinguishing properties such as low, variable refractive indices and fibrous appearance or undulose extinction. In addition, it is commonly brown in transmitted light, biaxial, chemically more reactive than quartz, and shows suppression of the low–high transition of quartz as commented on by Peltó (1956).

A variety of silicate minerals are known to occur as secondary cavity-filling deposits, especially in the volcanic basaltic terrains (Chemtomb and Rossman 2014). The Deccan traps basaltic lava flows almost invariably contain amygdals filled with crystalline and cryptocrystalline silica along with other minerals, especially zeolites (Sukheswala *et al.* 1974) and calcite (Ottens 2003). The crystalline minerals within the Deccan traps received much attention due to their aesthetic value and usefulness as precious/semi-precious stones. The cryptocrystalline silica, on the other hand, remain neglected notwithstanding their consistent and profuse occurrence throughout the Deccan LIP. However, recent researches have demonstrated their utility as the indicator of the chemical weathering of basaltic rocks and the palaeoenvironments (Chemtomb and Rossman 2014). Moreover, they find an exclusive importance in the study of the composition of the Martian surface (e.g., Kraft *et al.* 2003; Skok *et al.* 2010).

It is in this view that the present research work has been undertaken. In this study, the characterisation of amorphous silica occurring within Deccan trap basaltic lava flows of the Nagpur city and surrounding areas has been attempted. However, major emphasis has been placed on the freshly exposed samples from the dug well cuttings towards the northern foothill side of the Laxminarayan Institute of Technology (LIT) hill, LIT Campus, RTM Nagpur University.

2. Geology of the area

Nagpur city (21°09'N; 79°07'E), covering an area of about 100 km², is situated at an altitude of over 290 m above the mean sea level. However, there is a general increase in ground elevation of about 350 m towards the western part of the city. Geomorphologically, the area is occupied by denudational hills, dissected pediments and pediplains (Gwalani and Dalal 1988; Subramanyanan *et al.* 1996).

The geology of Nagpur city has been studied in detail by Pande *et al.* (1969), Deshpande (1998) and Subramanyanan *et al.* (1996), and, more recently, the geological information was compiled by GSI (2000) on a regional scale. The following discussion is based mostly on the above references; a summary of the geology of Nagpur city is given in table 1. The geological formations observed within Nagpur city (figure 1) include Precambrian crystalline metamorphic rocks, Permo-Carboniferous Lower Gondwana sediments, Upper Cretaceous Lameta sediments and Cretaceous–Palaeogene Deccan trap basaltic lava flows separated by intertrappean beds along with recent alluvium of the Nag and Peoli rivers. A detailed description of these rock formations is given below.

2.1 Precambrian metamorphic rocks

The Precambrian crystalline metamorphic rocks are represented by ortho-gneisses, streaky gneisses, amphibolites, marbles and pegmatites of the Sausar group. They are exposed between the

Mahadula and Suradevi, and Khaperkheda and Koradi. Metamorphics are also exposed near Bardi, Itwari, Indora, Pardi and Kalamna (figure 1); however, due to the thick population density, none of the outcrops are preserved. These formations are only exposed during excavation for dug well or drill holes. The Precambrian rocks lie concealed below the younger formations, and their direct contacts are occasionally seen with Gondwana sediments or Lameta formations, but rarely with the Deccan traps.

2.2 Gondwana supergroup

The rocks of the Lower Gondwana formations comprising Talchir, Barakar and Kamthi formations are exposed. Their dips commonly vary between 15° and 20° due SW to SSW. Green-coloured Talchir shales and basal conglomerates (tillites of glacial origin) are exposed towards the eastern side of the Koradi temple near a railway track adjacent of the Suradevi hills, as well in a stream section towards the north of Nagpur. Although no surface exposures of the Barakar formation are available, they are often encountered in the dug well and nala cutting sections below Kamthi sandstones. However, Barakar sandstones lie beneath the alluvium of the Kanhan river. Kamthi formation comprises ferruginous laminated sandstones, interbedded with reddish, white and buff coloured laminated shales. Their exposures are available near Jaripatka, Bokhara, Nara and Kalamna (figure 1). These sediments are found in direct contact with the Precambrian metamorphic

Table 1. Geological units occurring in Nagpur city (modified after Subramanyanan *et al.* 1996).

Geological time unit	Lithostratigraphic unit	Approx. max. thickness (in m)	Description
Recent to Quaternary	Alluvium and soil	10	Predominantly gravel, sand, silt and clay
Lower Eocene to Upper Cretaceous	Deccan traps and the intertrappean bed	48	Two basaltic lava flows separated by intertrappean beds; compact to vesicular, amygdaloidal, at places highly weathered and jointed basalts Green earth, calcareous and fossiliferous clayey and marly sediments
Upper Cretaceous	Lameta formation	15	Sandstones, earthy, red and white, silicified limestones
Upper Permian	Kamthi formation	168	Sandstones, shales and ferruginous (ochre, reddish, brownish coloured) sandstones
Lower Permian	Barakar formation	140	Sandstones, shales and carbonaceous shales
Upper Carboniferous	Talchir formation	>20	Green shales, boulder beds (tillites)
Archaean	Sausar group	–	Mica-schists, quartzites, marbles, streaky- and ortho-gneisses

Figure 1. Geological map of Nagpur city and surrounding areas (modified after Pande *et al.* 1969; Gwalani and Dalal 1988; Subramanyan *et al.* 1996).

rocks belonging to the Sausar group; although the contact is often faulted. Typical lower Gondwana plant fossils are found at these localities, especially Silewada ($21^{\circ}12'22''\text{N}$; $79^{\circ}07'30''\text{E}$) and Bokhara ($21^{\circ}15'58''\text{N}$; $79^{\circ}08'82''\text{E}$).

2.3 Lameta formation (*infratrappean*)

Lameta formation comprises white to off-white limestones with thin bands of sandstones and clays. A good population of fossils including vertebrate fossils and remains of dinosaurs are known to occur in the Lameta formation elsewhere (e.g., Mohabey and Udhoji 1996), although no records of their availability within Nagpur city area are available. The rocks belonging to the Lameta formation were seen in most dug wells in Dharampeth, Itwari and Sadar areas. They were also exposed in excavations made for laying pipelines and building foundations in many areas including Sri Mohini Complex, Sadar and Road Transport Office (RTO), Civil Lines. At these places, Lametas were buried under the soil cover and the overlying orthogneisses (Subramanyan

et al. 1996). The Lameta beds have been affected by a series E–W trending faults post the Deccan trap age (Pande *et al.* 1969).

2.4 Deccan traps and intertrappean beds

More than half of the city area, especially the western and the southern parts, is covered by the Deccan traps basaltic lava flows. A centrally situated step-like linear belt comprising the Lameta formation (figure 1) marks the boundary between older rocks and younger lava flows. The Deccan traps comprise a series of basaltic lava flows with each flow having a massive unit at the bottom and a vesicular unit at the top of the flow. Individual flows are separated by the sedimentary (clay or shale) parting of intertrappean beds. The basaltic lava flows are usually dark grey, compact, fine-grained with clinker surfaces, irregular vesicles and fragmentary tops, resembling ‘aa’ type flow surfaces. They are well jointed and weather into angular to sub-rounded blocks. At some places, such as the LIT hill, prismatic columnar joints are exposed (figure 2a).

Figure 2. (a) Section of LIT hill exposing lower basaltic lava flow. Prominent columnar jointing pattern is seen. (b) Highly vesicular portion of the lava, most of the cavities are unfilled. Note that many of the cavities are irregular, elliptical and elongated. (c) An amygdaloidal portion of the lava. Here most of the cavities are filled with secondary silica, such spherical, pear- and almond-shaped, pea-sized silica nodules get detached from the main rock and profusely occur in the overlying soil/detritus. (d) Irregular cavities with silica infilling is seen. Also, note small veins indicating pathways for the flow of silica-rich solutions. (e) Typical pattern of cavity filling within the Deccan traps basaltic lava flows.

2.5 Intertrappean beds

The intertrappean beds of Nagpur are well studied, especially for their fossils. It is the type locality for the fresh water mollusks, notably, *Physa principia* (Hislop and Hunter 1855). The intertrappean sediments are exposed near Takli, Telankhedi, Ambazari, Ramnagar, Ramdeobaba hill and Dabha. However, recently exposed sections at Dhapewada and Mahurzari just at the fringe of Nagpur city are spectacular still today.

3. Sampling and analysis

To address the several traverses of the study, several traverses were made within the city limits and adjoining areas, but freshly exposed, sizable and un-weathered samples were difficult to obtain. However, a recently dug well in the premises of LIT (21°08'44"N; 79°02'55"E), RTM Nagpur University Campus, provided fresh samples of secondary silica (figure 2b–e). The samples ($n = 3$) were carefully separated and cut to form thin and polished

sections. Another chunk of the samples were finely powered and sieved, an ASTM of 200 mesh size. Among the samples selected, one of the samples was used for analyses using different techniques as mentioned below.

The X-ray diffraction (XRD) analysis of chalcedony was performed on a Panalytical X'Pert Pro (model-PW 3040/60) diffractometer with CuK α radiation ($\lambda = 1.54 \text{ \AA}$) generated at a voltage of 40 kV and a current of 40 mA. Scanning was done in the 2θ angle of $5\text{--}80^\circ$ with a scan step size and time per step of 0.01° and 15 s, respectively. The morphological changes were investigated using a scanning electron microscope (SEM-JEOL 6830A). Prior to the study of surface morphology, the material was coated with a thin platinum coat using auto sputter (JOEL-JFC 1600 auto fine coater) to help the material conduct to obtain the images. Fourier transform infrared (FTIR) spectra of the samples were recorded using a Perkin Elmer Spectrum One FTIR. Potassium bromide (KBr) was used for collecting the background and a total of 20 scans were taken. The thermogravimetric differential thermal analysis (TGDTA) graph was generated using a thermogravimetric differential thermal analyser (Perkin Elmer Diamond TG/DTA), and the sample was heated from room temperature to 1000°C at the rate of $10^\circ\text{C}/\text{min}$. Argon gas was perched for maintaining the inert atmosphere so as to avoid oxidation of the sample.

4. Results

4.1 SEM analysis

The SEM images indicate dominantly fibrous morphology at lower magnifications (typically less than $3500\times$; figure 3a–c) and grainy morphology (on the surfaces) at very high magnification (more than $4000\times$, more prominently at $8000\times$; figure 3d–f). Similarly, the XRD pattern coupled with high-magnification imaging by SEM indicates the presence of length-fast chalcedony in which crystallites are stacked perpendicular to the c -axis with the fibres twisted around the elongation axis and also indicating the overlapping of grainy over fibrous morphology.

4.2 XRD analysis

The results of the X-ray diffractometric study and the diffractogram is presented in figure 4. The peak

intensities corresponding to 2θ angles are located at 20.76° , 26.57° , 36.51° , 39.41° , 42.35° , 50.05° , 59.86° and 68.05° . The grain size was estimated using the Debye–Scherrer formula

$$D = \frac{0.9\lambda}{B \cos \theta},$$

where D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, λ is $1.54 \text{ \AA}$ for the wavelength of CuK α radiation, B is the full-width at half-maximum and θ is the Bragg's angle.

Substituting values in the above formula, an overall size of the particles of crystal was calculated to be $\sim 22.61 \text{ nm}$. It is clear from figure 4 that in the 2θ range from 20° to 70° there are at least six conspicuous peaks which can be indexed only on the hexagonal cells of chalcedony. In length-fast chalcedony, the grains appear to be stacked perpendicular to the c -axis, and along the a -axis, the virtual fibre axis is either (1120) or (1010) (Braitsch 1957). The preferred growth direction seems to be along (1010) in the sample, hence the sample is a length-fast chalcedony.

4.3 DTA and TGA analyses

DTA and TGA analyses and heat flow (DTA) and weight loss curves (TGA) are shown in figure 4. The results of these studies are discussed below.

4.3.1 Differential thermal analysis

An initial endothermic peak is observed at 41.113°C at which the heat flow through the sample was about -3.082 mW . With the increasing temperature, there is a continuous rise in heat flow until it reaches a peak temperature of 206.113°C and the corresponding heat flow of 0.829 mW . Further increase in temperature does not show much change with only a minor decrease in heat flow until it reaches 606.113°C , where a major inflection of 0.852 mW is observed. Based on this curve (figure 5), two major inflection points were theoretically calculated. The first one corresponds to an endotherm of $\sim 173.85^\circ\text{C}$ and the second one corresponds to that of 603.92°C . These temperatures indicate that the mineral is broadly endothermic in character; the sharp endothermic peak at 603.92°C probably corresponds to dehydroxylation reactions.

Figure 3. SEM images showing various morphological and textural features: (a) fibrous and bladed morphologies of chalcedony (magnification: 370 $\times$). (b) A closer view of the surface shows somewhat coalesced fibres, the alignment of which is overshadowed by chonchoidal to subchonchoidal fractures formed due to the powdering of mineral (magnification: 1300 $\times$). (c) bladed chalcedony overprinted with grainy morphology (magnification: 3500 $\times$). (d) Another crystal showing fibrous and bladed morphology, with little coalesced fibres (magnification: 3500 $\times$). (e) A crystal showing dominantly grainy morphology at higher magnification (magnification: 4000 $\times$). (f) Highly magnified view of the same crystal demonstrating grainy morphology with directional fabric developed. Such a feature indicates that both fibrous and grainy morphologies are simultaneously present in the mineral under study (magnification: 8000 $\times$).

4.3.2 Thermogravimetric analysis

The TGA curve is much more complex and undulating compared to known samples (Parali *et al.* 2015). Here four major events of mass losses corresponding to temperatures of $\sim 37^{\circ}\text{C}$, $\sim 190^{\circ}\text{C}$, $\sim 580^{\circ}\text{C}$ and $\sim 850^{\circ}\text{C}$ were observed. The weight-loss at the starting temperature is due to the loss of absorbed moisture by the sample. The second weight-loss ($\sim 190^{\circ}\text{C}$) may correspond to the loss of structural water. The third and fourth events of weight-loss are rather continuous, but prominently observed due to the drastic change in the slope on the curve (figure 5) between $\sim 580^{\circ}$ and $\sim 760^{\circ}$,

and $\sim 850^{\circ}$ and above. The last two weight-losses might correspond to the dehydration of the silanol (SiOH) group water from chalcedony (Hatipoglu *et al.* 2010).

4.4 FTIR analysis

The FTIR spectrograph of the sample shown in figure 6 was collected in the range of 450–4000 cm^{-1} , as it was taken to confirm the presence of the functional group of the sample. The intense peak at wavelength 1105 cm^{-1} is estimated to match with the characteristics peak of the Si–O

Figure 4. XRD pattern for the chalcedony sample analysed during this study (inset).

Figure 5. Thermal analysis chalcedony with DTA (blue) and TGA (red) curves.

Figure 6. FTIR reflectance data of the secondary silica. Significant peaks are marked on the diagram.

aliphatic stretch, whereas the broad peak at wavelength 3453 cm^{-1} confirms the presence of the OH bond. The Si-O out-of-plane vibration is confirmed from the peak at 458 cm^{-1} and the peak at 800 cm^{-1} confirms the Si-OH stretch (Pavia *et al.* 2001).

5. Discussion and conclusions

5.1 Nomenclature and characterisation

Quartz (SiO_2) has been traditionally classified into three general varieties, namely, *macrocrystalline* (varieties that develop visible crystals or are made of large intergrown crystals; macro-large), *microcrystalline* (compact varieties made of tiny crystal grains that are visible in an optical microscope; micro-small) and *cryptocrystalline* (dense varieties whose structure cannot be resolved using an optical microscope; crypto-hidden). The macrocrystalline varieties of silica are comprehensively called as ‘quartz’, whereas cryptocrystalline varieties are subsumed under the term ‘chalcedony’. Low but variable refractive indices, fibrous appearance and undulose extinction are certain distinguishing optical properties of chalcedony (White and Corwin 1961). Varieties of macrocrystalline quartz include: rock crystal, amethyst, ametrine, aventurine, blue quartz, citrine, eisenkiesel, milky quartz, pink quartz, prase, prasiolite, rose quartz, smoky quartz, tiger’s, hawk’s, and cat’s eye. Crypto- and microcrystalline quartz occur in two optically distinguishable varieties, namely, (i) *fibrous chalcedony* (agate, carnelian, chalcedony, chrysoprase, onyx and sard and (ii) *grainy chalcedony* (chert, flint, heliotrope and plasma). The above distinction between fibrous and grainy varieties is based on the visual appearance of a thin section under a polarising microscope. Based on the conspicuous behaviour of chalcedony in polarised light, at least two types can be distinguished in thin sections (Michel-Lévy and Munier-Chalmas 1892; Correns and Nagelschmidt 1933; Braitsch 1957; Frondel 1978; Flörke *et al.* 1991), viz., length-fast chalcedony with crystallites stacks perpendicular to the *c*-axis wherein the fibres may be twisted around the elongation axis (Miech *et al.* 1984) and length-slow chalcedony or quartzine with crystallites stacked parallel to the *c*-axis (Flok and Pittman 1971). Recent studies based on SEM, transmission electron microscopy, selected area electron diffraction, etc. have demonstrated that both fibrous and grainy varieties of quartz consist of

microscopically small intergrown crystal grains (Monroe 1964; Frondel 1978; Graetsch 1994; Cady *et al.* 1998; Lynne *et al.* 2007; quartzpage.de.html).

It is, however, generally agreed that the macro-crystalline quartz grows by adding molecules layer by layer, whereas cryprocrySTALLine chalcedony forms a colloidal watery solution of silica (Akhavan 2012), although some varieties such as chert, sinter, flint, jasper, etc., do not strictly fit into the above definition. Similarly, we were unable to distinguish our sample fitting into the above nomenclature, therefore, preferred to use a general term, chalcedony.

5.2 Secondary silicates mineralisation in the basalts of the Deccan traps

During the Cretaceous and the Tertiary periods, large parts of the present subcontinent of India were flooded by multiple lava flows. Seismological investigations have shown that the total remaining thickness in the north-east of the volcanic province is now about 100 m and at the elevations along the west coast up to 1500 m. The lavas rose up through several fissures of the Earth's crust and flowed over large areas. As the lava cooled, many small, but also some large up to 100 cm across gas blisters and vesicles were preserved. At a later, post-volcanic time, these cavities were in-filled with calcium-rich silicates as well as with quartz and calcite that precipitated from hot aqueous solutions passing through the basalts. The chemical nature of these hydrothermal solutions was determined by the composition of the basalt, the length of contact with the basalt and the temperature (Deshmukh and Nair 1996).

The basalts of the Deccan traps have high calcium content, low magnesium and aluminium content, and an average SiO₂ content of about 50%. As the temperature of these solutions fell below 300°C, clay minerals and chlorite get crystallised (Gottardi and Galli 1985). With the temperature sinking to 200–100°C, prehnite, natrolite and laumontite followed. At temperatures of 110–90°C, heulandite, stilbite and apophyllite developed, and at 90–60°C, mesolite and scolecite formed. Finally, the low-temperature zeolites, thomsonite and chabazite crystallised (Ottens 2003).

Earlier workers have studied the zeolites from Deccan LIP. A systematic study of the secondary silicates provided possible zonation of zeolites within the lava flows (Sukheswala *et al.* 1974).

However, a subsequent study from the Western Ghats (Jeffery *et al.* 1988) has rejected the hypothesis of zeolite zonation. Although zeolite is one of the most commonly occurring secondary silicate along with quartz and chalcedony within the Deccan LIP, it occurs in relatively minor quantity within lava flows of the eastern Deccan traps. It is, however, understood that the secondary minerals in the Deccan traps were precipitated from fluids that migrated through the basalts, and there is evidence that most of the zeolites were formed at temperatures below 150°C (Jeffery *et al.* 1988; James and Walsh 1999). It is also assumed that the fluid was meteoric ground water rather than hydrothermal in origin, and that the dissolved materials in the fluids must have come from fluid–rock interaction (Parthasarathy 2006).

It had been demonstrated earlier that chalcedony and quartz were formed rapidly at 400°C (White and Corwin 1961); however, chalcedony gets converted to fibrous quartz and cannot persist any further. It was postulated that such transformations should take place at temperatures as low as 300°C (Kennedy 1950; Carr and Fyfe 1958; White and Corwin 1961) and complete conversion of amorphous silica to quartz was observed at ~250°C. Therefore, the upper limit for the formation of chalcedony was suggested to be 300°C. On the other hand, mineral opal is present at lower temperatures below 100°C, whereas quartz could not form below 100°C. White (1955) noted that opal is replaced by chalcedony and quartz in hot spring deposits at temperatures greater than 100°C. However, White *et al.* (1956) noted that opal could form at higher temperatures such as ~140°C, but it is unstable and changes to chalcedony and quartz, suggesting that the lower temperature limit of chalcedony is above 100°C. Thus, the order of formation and persistence of chalcedony is within a range of 100–300°C. Therefore, we assume that the deposition of chalcedony of the Deccan trap basalts should be within this temperature range.

Water-rich solutions are necessary for the formation of chalcedony. The nature of these solutions is of critical importance in determining whether chalcedony and quartz will form in a given time interval, or whether amorphous silica or crystallite will persist. The hydrogen ion concentration (pH) is an important factor in this regard. Opal is considered to be a disordered low crystallite. The sequence of changes of the various hydrous

silica polymorphs shown is: amorphous silica (or opal) → crystoballite → chalcedony (or micro-crystalline quartz). Similarly, it was noted by Braitsch (1957) that crystoballite gets converted to chalcedony, and that the ‘silica gel’ may change to cristobalite–opal or directly to chalcedony; or in some instances crystoballite–opal changes to chalcedony. Therefore, in conclusion, most chalcedony and chert are secondary products and require the former presence of gelatinous silica (Krauskopf 1956, 1959; White and Corwin 1961). During the present study, it was observed that the dominant cavity-filling minerals are quartz and chalcedony, which indicates a temperature range of ~100–300°. The relative absence of opal and crystoballite in the cavities (amygdules) probably indicate that the mother fluid was a hot aqueous solution that crystallised as chalcedony and crystalline secondary quartz within the Deccan traps of Nagpur city.

5.3 Genesis of hydrous amorphous silica

Hydrous amorphous silica is a common product of incongruent chemical weathering of basalt glass and basalt-associated minerals; therefore silica coatings are frequently observed in other basaltic terrains (Gordon and Dorn 2005; Fulignati *et al.* 2006; Prinsloo *et al.* 2010). Silica coatings are also frequently observed in arid deserts (Weed and Ackert 1986; Perry *et al.* 2006) as well as anthropogenically altered terrains (Schindler *et al.* 2009; Durocher and Schindler 2011; Mantha *et al.* 2012). These were suggested to occur even on the surface of Mars (Kraft *et al.* 2003; Skok *et al.* 2010).

Various mechanisms have been proposed for the formation of silica coatings and cements e.g., Hawaiian flows, such as:

- (1) dissolution–reprecipitation of near surface glasses (Minitti *et al.* 2007; Hellmann *et al.* 2013);
- (2) dissolution–reprecipitation of windblown particulates (Farr and Adams 1984; Curtiss *et al.* 1985); and
- (3) transport and deposition of externally derived Si in solution (Schiffman *et al.* 2006).

However, the timing and the rate of coating of the formation are poorly understood. The dissolution rates of basaltic glass have been studied experimentally by many researchers (Oelkers and Gislason 2001; Gislason and Oelkers 2003; Tosca

et al. 2004; Wolff-Boenisch *et al.* 2004; Hurowitz *et al.* 2005; Gudbrandsson *et al.* 2011). However, *in-situ* weathering rates may be orders of magnitude lower than those measured experimentally (White and Brantley 2003).

It has been demonstrated earlier that the silica-rich coatings may form on basalt over long time periods under neutral pH conditions (Dorn 2012); however, recent studies show that such coatings might be formed by the interaction with acidic fluids and vapours (Chemtomb and Rossman 2014). For instance, the high sulphur content of Kilauean silica coatings, primarily present as jarosite (Minitti *et al.* 2007; Chemtob *et al.* 2010) indicated that SO₂ was the primary volcanically derived acid source involved in coating formation. The analogy is equally applicable to the Deccan trap basalts, in which, the following were proposed to be the sources of acids and sulphur: volcanically derived acids, including local fissure vents, regional plumes and volatiles degassed from the lava itself. The presence of sulphur within the Deccan magma has been amply demonstrated, e.g., Randive *et al.* (2015). More detailed sampling covering a larger area might help in understanding the nature of mother fluid which crystallised secondary silica all over the Deccan plateau.

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