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ORIGINAL ARTICLE

Oxygen and hydrogen isotope ratios of chert from the Sixtymile Formation in Grand Canyon National Park, USA: a warm palaeoclimate, freshwater deposit

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Abstract New oxygen and hydrogen isotope ratios of chert from middle, intraformational breccias, and upper breccia members of the Sixtymile Formation (SMF) in eastern Grand Canyon National Park (AZ) yield palaeoclimate estimates between 27 and 33 °C. The isotopic compositions of cherts define a domain approximately parallel to the meteoric water line when plotted on a δD–$\delta^{18}O$ diagram; these data indicate that meteoric water was involved during formation of the chert. In thin section, the absence of interlocking mega quartz (>35 μm) and silica-filled fractures and veins, along with preserved micromorphological silica fabrics, suggest that the chert has not been permeated by later hydrothermal fluids. Petrographic observations in thin section such as cyclic silica precipitation phases and glaebular micromorphologic fabrics lend support to the interpretation that meteoric waters were involved during chert precipitation. The post 742 Ma SMF has been correlated with diamictite (transition) beds of the Kingston Peak Formation (CA), which in turn have been interpreted to have been deposited during the Sturtian Ice Age (~750–700 Ma). Absence of facetted and striated clasts and other diagnostic glaciogenic features in the SMF, an unconformable contact with the stratigraphically older Chuar Group, coupled with warm palaeotemperature data inferred from stable isotope values of chert, tentatively suggest that deposition of sediment in the SMF likely did not take place during the Sturtian Ice Age.

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1 Introduction

The Sixtymile Formation (SMF) is important because it occupies a time in Earth history that is poorly-represented in Grand Canyon National Park (GCNP), northern Arizona and southwestern USA. The SMF rests unconformably above the Neoproterozoic Chuar Group, is unconformably overlain by the Middle Cambrian Tapeats Formation (515–505 Ma; Kirschvink et al. 1997) and crops out in only four isolated, spatially-limited, relatively inaccessible locations in eastern GCNP (Fig. 1; Timmons and Karlstrom 2001). The SMF consists of laterally continuous, fine-grained, flat-bedded red sandstone (Fig. 2) alternating with recurrent lenses of white chert (Fig. 3) and thin (~0.3 m thick) intraformational lenses of breccia; this sequence is stratigraphically overlain by a chert-rich breccia (Ford and Breed 1973; Elston 1979; Timmons et al. 2001). Elston (1979) divided the SMF into lower, middle and upper members and speculated that the thin-bedded chert of the middle member was precipitated in "quiet, standing water". Elston (1979) also suggested that the upper member of the SMF which contains shattered, angular rock fragments was likely derived from the middle member (Fig. 4). Timmons et al. (2001) reevaluated the SMF stratigraphy and suggested that the lower member of Elston (1979) was better correlated to the stratigraphically older, uppermost Walcott Member of the underlying Neoproterozoic Chuar Group. Both Elston (1979) and Timmons et al. (2001) interpret the middle and upper members of the SMF as non-marine deposits. Dehler et al.

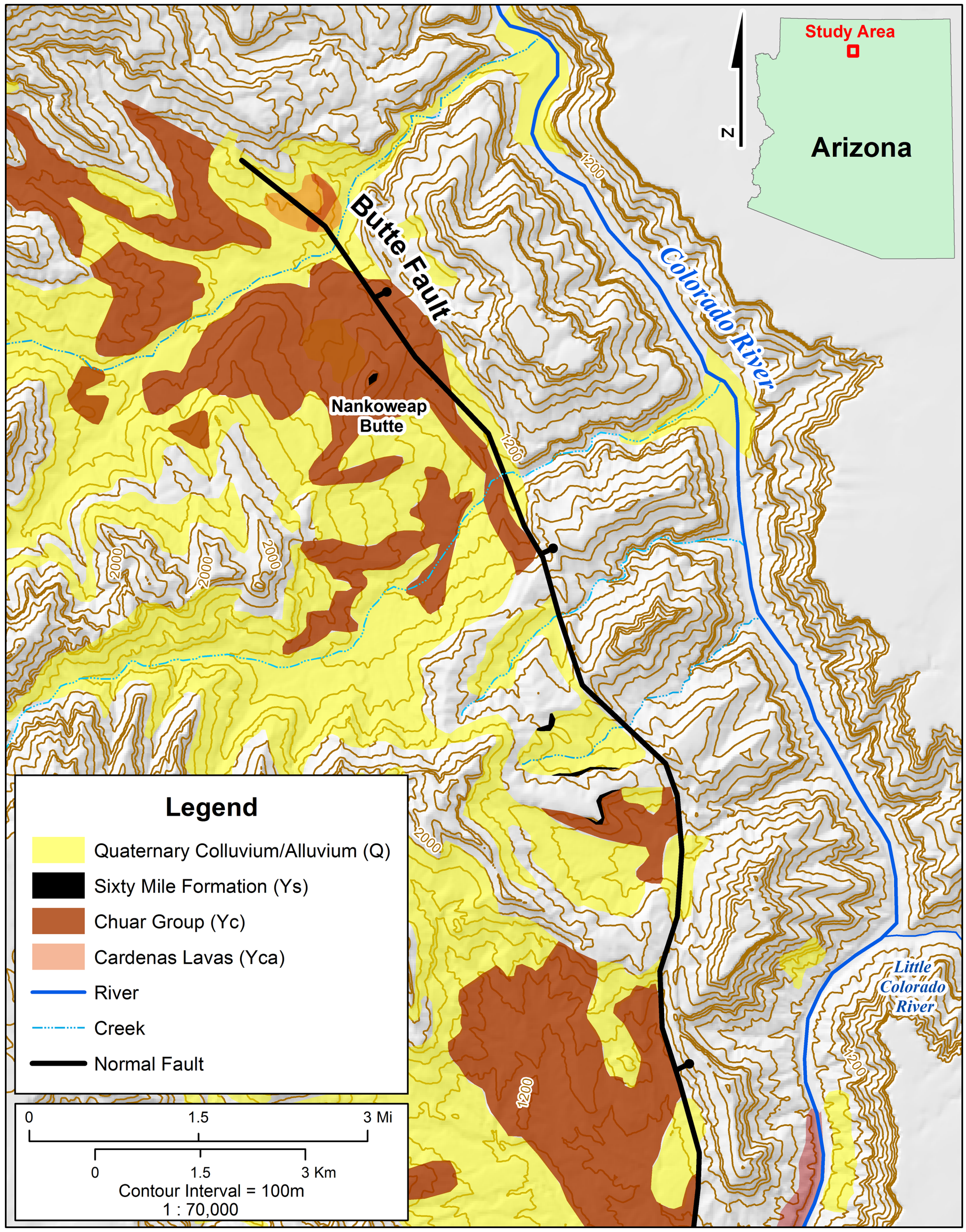

Fig. 1 Nankoweap Butte study site location map. Sixtymile Formation and Chuar Group stratigraphy

(2001) indicated that the sediments of the underlying the Neoproterozoic (~800–742 Ma) Chuar Group were deposited in a marine cratonic basin. Karlstrom et al. (2000) provided the first U–Pb age of the Walcott Member of the Chuar Group (742 ± 7 Ma) from an ash layer approximately 1 m below the erosional contact with the overlying SMF. The SMF therefore likely represents a notable change from a marine depositional environment to a continental/terrestrial depositional environment. To date, no definitive, quantitative evidence of a terrestrial depositional environment for the SMF has been reported.

The absolute age of the SMF is presently unknown. The sedimentary rocks of the SMF post-date the 742 ± 7 Ma age assigned to the underlying Walcott Member (Chuar Group; Karlstrom et al. 2000; Karlstrom and Timmons 2012) and pre-date the basal conglomerates of the Cambrian Tapeats Sandstone (515–505 Ma). Elston (1979) considered uplift of the marine cratonic basin (Chuar Group sedimentation) to have taken place ca. 820 Ma. Timmons et al. (2001) suggest that progressive rifting occurred between 800 and 742 Ma and the syntectonic SMF was likely deposited during extension of western North America associated with the breakup of western Laurentia. Link et al. (1993), following the lithostratigraphic framework proposed by Young et al. (1981), inferred that the SMF may correlate with the diamictite (transition) beds of the lower Kingston Peak Formation (Pahrump Group) in southern California. The diamictite

Fig. 2 Sixtymile Formation outcrop at Nankoweap Butte. The Sixtymile Formation at Nankoweap Butte is a the laterally-continuous, fine-grained, flat-bedded red sandstone with abundant white chert lenses

Fig. 3 Laminar chert beds; middle member of the Sixtymile Formation (ruler length ~9 cm)

beds of the Kingston Peak Formation have been interpreted to represent glaciomarine and glaciofluvial (tillite) deposits of the global Sturtian Ice Age (~750–700 Ma; Labotka et al. 1980; Miller 1985; Prave 1999; Corsetti et al. 2003).

Fig. 4 Chert breccia in the upper member of the Sixtymile Formation (hammer head is ~18 cm long)

However, preliminary field work on the SMF in Grand Canyon indicates a complete lack of facetted and striated clasts, glacially-polished clasts and other diagnostic glaciogenic features, which suggests that the SMF may not be a chronostratigraphic equivalent of the Kingston Peak Formation tillites. Obtaining quantitative evidence on the palaeoclimate of the SMF will help determine whether the SMF was deposited during the Sturtian Ice Age and correlative with the Kingston Peak Formation diamictites.

2 Research hypothesis and approach

Oxygen and hydrogen isotopic compositions of silica have been successfully used to better understand the crystallization history of silica because once the granular, microcrystalline quartz has crystallized the isotopic composition is preserved (Knauth and Epstein 1976). Crystallization temperatures and the role of meteoric waters in the initial crystallization of silica can be discerned from the stable isotope values. The research hypothesis of this study is that SMF chert did not precipitate during cold climate conditions. Oxygen and hydrogen isotope ratios of bedded chert, intraformational chert breccia, and chert breccia from the upper member of the SMF were used to determine approximate quartz crystallization temperatures and whether meteoric or marine waters were involved in the crystallization history of the chert. Chert petrography was used to provide additional clues to the depositional environment and to assess possible post-depositional alteration of the chert.

Permission to collect samples from Nankoweap Butte (eastern GCNP) was authorized by the National Park Service (research permit #GRCA-2015-SCI-0002). Oriented field samples were collected from the middle member of the SMF and non-oriented chert samples were collected from the upper member and intraformational breccia. In the lab, millimeter-size (usually ~4 mm) interior chert chips were hand-quarried from field samples. The millimeter-size sample chips were visually inspected and analyzed under a binocular microscope for the presence of iron-oxides or other macro impurities. A hand-held magnet was passed over the samples to detect and remove any (magnetic) iron-oxide. Samples determined to be free of impurities were selected for isotope analysis. Oxygen and hydrogen isotope analyses were conducted following the well-established, in situ laser extraction method of Sharp (1990) and Sharp et al. (2001) in the University of Texas at Austin stable isotope lab. Thin sections were prepared in the Geosciences research lab at Fort Lewis College.

3 Results

Oxygen and hydrogen isotope ratio data for twenty-one cherts from the SMF at Nankoweap Butte are shown in Fig. 5; the data are given in Table 1. All data are reported relative to V-SMOW in standard δ-notation. $\delta^{18}O$ values represent total (structural) oxygen in chert and silica; δD values are derived from non-surface hydroxyl groups extracted from within the chert. All analyses have a precision of ±0.2‰ and ±2‰ for $\delta^{18}O$ and δD, respectively.

The oxygen and hydrogen isotope ratio data derived from the SMF cherts form domains elongated away from Line A on a δD–$\delta^{18}O$ diagram (Fig. 5). Line A is the inferred locus of isotopic compositions of cherts in equilibrium with modern sea water at various temperatures (Knauth and Epstein 1976). Chert data are interpreted in terms of palaeotemperatures by comparing them with temperature lines drawn approximately parallel to the meteoric water line (Fig. 5) as established by Knauth and Epstein (1976). Chert data elongated away from Line A indicate that meteoric (fresh) waters were involved in the crystallization history of the chert. Palaeotemperature estimates for the SMF chert range from about 27 to 33 °C. The chert data suggest that the palaeoclimate at the time of chert precipitation was warm and therefore, is inconsistent with precipitation under cold "snowball" Earth temperatures and environmental conditions. No significant isotopic distinction was observed between the upper breccia member and the middle laminated chert member of the SMF (Figs. 3, 4).

In thin section, silica forms complex micromorphological fabrics; both radial and fibrous length-slow (Quartzine) and length-fast (Chalcedony) occur (Fig. 6), however length-slow (Quartzine) is not abundant. Silica occurs as mosaic, microgranular (<35 μm) quartz and forms: (1) colloform crusts (Fig. 6); (2) glaebular aggregates (Fig. 6); and, (3) both fine and wavy laminae (Fig. 6). Laminae overlying silica nodules in oriented chert samples are occasionally disrupted by fine-cracks (Fig. 6). Opaque minerals (titania) occur infrequently and randomly as secondary minerals. No mega quartz (>35 μm) or thermally annealed or obliterated silica fabric was observed in thin section. Silica-filled veins and phyllosilicate minerals were similarly absent.

4 Discussion

Analyses of oxygen and hydrogen isotope ratios of chert have yielded reasonable and reproducible palaeoclimate estimates that have been independently verified with proxy data which are resistant to alteration and isotopic exchange, including clay minerals and iron-oxyhydroxide material (Abruzzese et al. 2005). Oxygen and hydrogen isotopes of chert record the isotopic composition of total oxygen and trace hydroxyl groups preserved in silica and chert at the time of precipitation and crystallization (Knauth and Epstein 1976). Approximate palaeotemperature estimates based on analyses of oxygen and hydrogen isotope ratios of marine silica and chert are well established (Knauth and Epstein 1976; Knauth and Lowe 2003; Hren et al. 2009). Kenny and Knauth (1992) demonstrated that oxygen and hydrogen isotopic composition of secondary (authigenic) silica precipitated in palaeokarst chert lags could be used to estimate near-surface continental weathering temperatures. Kenny (2010) reported continental weathering temperatures inferred from oxygen and hydrogen measurements derived from secondary silica precipitated during a tropical karst event that developed on the Mississippian Redwall Limestone of northern Arizona (USA). Abruzzese et al. (2005) suggested that oxygen and hydrogen isotope ratios of freshwater chert could be used as an indicator of regional climatic variation in the Cenozoic. Despite the fact that silica and chert have been successfully used to estimate palaeoclimatic conditions, the temperature assignments made with the method of Knauth and Epstein (1976) are subject to several uncertainties. (1) The curve for quartz-water isotope fractionation with temperature is not known well for low temperatures. The temperature lines, used in this method (Fig. 5), are extrapolated from better understood, high-temperature, quartz–water curves. (2) Stable isotope values of early chert must be preserved through time. Microorganisms embedded in Precambrian chert attest to the chemical integrity and physical stability of silica (Schopf et al. 2007; Knauth and Lowe 2003). Remarkable preservation of microorganisms (e.g., Knoll 1992; Schopf 1993; Horodyski and Knauth 1994; Sugitani et al. 2007) and previous oxygen and hydrogen isotope ratio studies on chert by Kenny and Knauth (1992) suggest excellent preservation of original isotopic values of chert

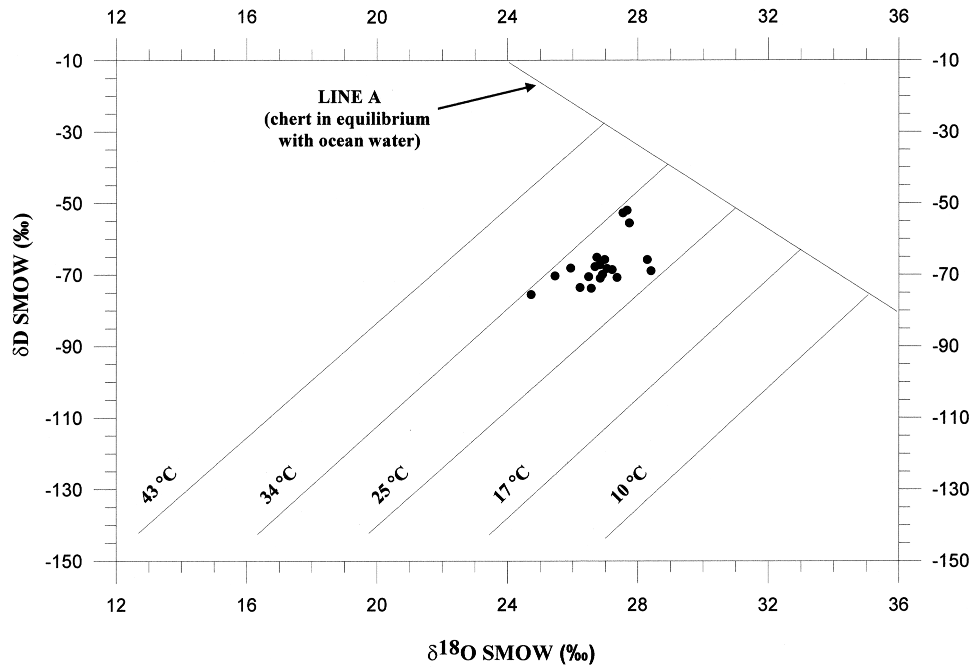

Fig. 5 $\delta^{18}O$ vs δD diagram. Climatic temperatures range from ~27 to 33 °C. Temperatures interpreted using the method of Knauth and Epstein (1976). Isotopic values also indicate that chert precipitated under fresh water conditions. Reproducibility for $\delta^{18}O$ is ±0.2‰ and δD is ±2‰. Reproducibility is based on duplicate runs and standards

Table 1 Description, data and location of the (21) Sixtymile Formation chert samples

$\delta^{18}O$ SMOW (‰)[a]	δD SMOW (‰)[a]	Description and location of chert samples
27.08	−69.8	Dense tan-colored chert; upper breccia (top of butte)
26.77	−72.1	Dense chert; upper breccia (top of butte)
26.37	−72.5	Dense white chert; upper breccia (top of butte)
26.65	−68.6	Laminar chert—less dense; middle member
25.8	−68.2	Laminar chert—less dense; middle member
27.19	−73.7	Laminar chert—less dense; middle member
27.2	−69.3	Laminar chert; dense core; middle member
26.83	−71.2	Laminar, dense white chert; middle member
24.5	−74.5	Laminar chert, porous chert/silica; middle member
26.66	−68.1	Laminar chert—less dense; middle member
26.7	−65.7	Laminar chert—less dense; middle member
26.54	−70.0	Laminar white chert—less dense; middle member
27.48	−51.5	Grey dense chert from large clast; upper breccia
27.4	−52.8	White dense chert from another large clast; upper breccia
27.72	−57.1	Grey dense chert, large clast; upper breccia
27.25	−72.2	Large (~10 cm) white chert; upper breccia
26.87	−67.1	Another large (~10 cm) white chert; upper breccia
28.34	−70.7	Laminar chert, dense tan-colored; middle member
28.36	−69.4	Laminar dense white chert; middle member
25.36	−71.6	Laminar chalky, less-dense white chert; middle member
27.1	−69.8	Dense white chert; upper breccia

All samples from Nankoweap Butte (Point Imperial Quadrangle, AZ); approximate UTM coordinates for Nankoweap Butte: Z12, 420625 mE, 4013650mN

[a] Reproducibility for $\delta^{18}O$ is ±0.2‰ and δD is ±2‰. Reproducibility is based on duplicate runs and standards

dating from the Late Proterozoic. Brasier et al. (2002) argued that some of the oldest, previously reported bacterial microfossils from the ~3.5 Ga Apex Group chert may be geochemical artefacts; other Late Proterozoic microfossils preserved in chert have not been disputed. (3) The temperature estimates in Fig. 5 also depend on the

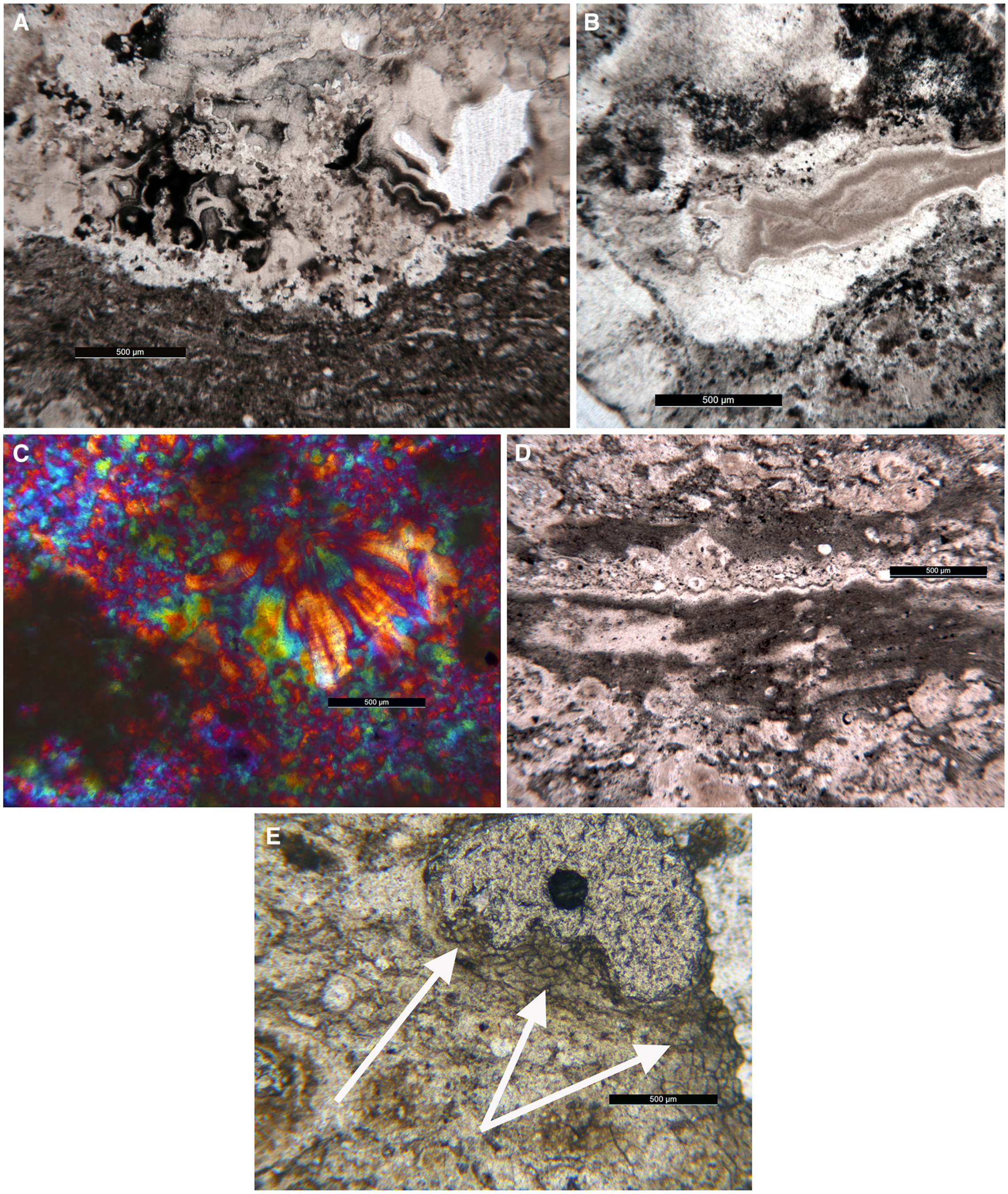

Fig. 6 Photomicrograph (plane polarized light; PPL) showing incremental silica replacement as successive colloform and ropy overgrowths (**a**) and isopachous vug fill (**b**). Alternating precipitation phases (possibly infilling solution voids) are indicative of alternating hydrologic fluxes (*scale bar* 500 µm). **c** Photomicrograph using a λ compensator showing length-fast Chalcedony surrounded by a ring of length-slow Quartzine (*scale bar* 500 µm). **d** Photomicrograph (PPL) illustrating finely-banded and the complex glaebular micromorphologic fabric suggestive of repetitive and fluctuating fluid flow episodes (inclusive of dissolution and precipitation events) (*scale bar* 500 µm). **e** Photomicrograph (PPL) of fine-grained laminae overlying silica nodules disrupted by fine cracks (*arrows*) perhaps resulting from dehydration of gel-like deposits (Iler 1979) (*scale bar* 500 µm)

assumption that $\delta^{18}O$ values of sea water have not changed significantly throughout geologic time. The generally lower $\delta^{18}O$ values of ancient carbonates (e.g., from the Silurian Period) have been used as an argument that $\delta^{18}O$ values of the past oceans were lower than modern values (Veizer et al. 1986; Veizer and Prokoph 2015). Knauth and Roberts (1991) provide arguments that they consider fatal to using carbonates to monitor the oxygen isotope composition of past seawater. Knauth and Roberts (1991) presented data, including direct analysis of unaltered ocean water preserved in salt deposits, which precludes the proposed ~5‰–6‰ oxygen isotope ratio changes in seawater as far back as the Silurian Period. In order to adequately determine the diagenetic history of carbonate samples used to monitor the oxygen isotopic composition of past seawater, both ^{13}C and ^{18}O co-variant values are needed. Veizer and Prokoph (2015) analyzed oxygen isotope ratios in carbonates to propose secular oxygen isotope ratio changes in ocean water during the Phanerozoic, but co-variant ^{13}C values for the oxygen isotope measurements have not been included in their published data set. Both ^{13}C and ^{18}O co-variant values are needed to determine if the platform carbonates are original precipitates, have been diagenetically altered at the molecular level, or have been partially altered by meteoric waters during the transformation of the host sediment into limestone (e.g., Knauth and Kennedy 2009). Zempolich et al. (1988) and Kenny and Knauth (2001) analyzed co-variant carbon and oxygen isotope ratios in Proterozoic Beck Spring (Pahrump Group) carbonates to argue that the Beck Spring ocean was not significantly different from modern sea water. Clumped isotope thermometry is a new approach that uses isotopologues (which are independent of the bulk isotopic composition) to examine the temperature dependence of bond formation between two rare, heavy isotopes within a single molecule to independently determine the $\delta^{18}O$ value of the fluid in a carbonate sample (Eiler 2007, 2011; Henkes et al. 2013). Cummins et al. (2014) used clumped isotope analysis to address the complicated uncertainties related to diagenetic alteration of $\delta^{18}O$ in carbonates used to estimate the oxygen isotopic composition of past seawater. Cummins et al. (2014) measured a large suite of well-preserved Silurian (ca. 433 Ma) carbonate fossils and determined that Silurian oceans had oxygen isotopic composition similar to the modern ocean. Clumped isotope research on non-icehouse carbonates from other geologic time periods has also been reported yielding similar results (Henkes et al. 2014). Collectively, the clumped isotope research largely supports previous studies by Knauth and Epstein (1976) and Knauth and Roberts (1991) which suggest that the $\delta^{18}O$ of Earth's ocean waters have remained broadly consistent through the Late Proterozoic. Additionally, assignment of temperature estimates by the Knauth and Epstein (1976) method are more sensitive to changes in $\delta^{18}O$ values than δD values. As such, palaeotemperature estimates based on oxygen and hydrogen isotope ratios of chert remain valid until a compelling argument can be presented to the contrary.

Enrichment of ^{18}O in chert may result if silica precipitation occurred under evaporative conditions. Abruzzese et al. (2005) documented a large range of oxygen isotope values (~20‰) in Eocene and Miocene Epoch chert which they attributed to large-scale changes in the isotopic composition of lake water due to evaporation. The relatively narrow range of oxygen values in the SMF cherts of this study (~4.5‰) suggest that evaporative processes were likely insignificant and evaporative enrichment was likely minimal during the crystallization history of chert.

O'Neil and Hay (1973) reported elevated oxygen isotope values from Magadiite cherts that formed in strongly saline lake deposits of East Africa. Oxygen isotope values in Magadiite cherts ranged from 33.8‰ to 38.3‰ and were determined to be compatible with precipitation from a brine and meteoric water mix (O'Neil and Hay 1973). No oxygen isotope values in the 33.8‰–38.3‰ range were obtained from this study suggesting that the cherts likely did not form in a saline-rich lake.

Elevated temperatures from post-precipitation metamorphic processes could produce low oxygen and hydrogen isotope values of chert and silica. Metamorphic processes capable of altering oxygen and hydrogen values also produce notable changes to silica, visible in thin section, including: (1) recrystallization of silica and the formation of mega quartz (>35 μm); and, (2) thermal annealing of laminar silica phases and other micromorphological silica fabrics. The absence of: (1) interlocking mega quartz (>35 μm) grains; (2) annealed fibrous and radial silica; and, (3) pervasive silica-filled veins, indicate that the chert has been minimally altered by hydrothermal activity, and that post-precipitation metamorphic processes and alteration of original stable isotope values is unlikely. Moreover, the inferred crystallization temperatures from the stable isotope values of the SMF chert are significantly cooler than if the chert had been pervasively altered by hydrothermal fluids. Hydrothermal fluids have been measured as low as (~100 °C) but are usually substantially hotter (Coumou et al. 2008). However, it remains a possibility that some stable isotope value degradation may have occurred given the antiquity of the samples.

Elston (1979) suggested that the upper member of the SMF which contains shattered, angular rock fragments was likely derived from the middle member. No significant isotopic distinction, nor petrographic distinction was observed between chert from the upper breccia member and the middle laminated member of the SMF (Figs. 3, 4). Based on the quantitative data from this research, it appears likely that chert in the upper breccia member of the SMF was indeed derived from the middle laminated member of the SMF.

In thin section, there are significant variations in the form and distribution of silica including repetitive silica phases (Fig. 6). Precipitation of repetitive silica phases usually requires either: (1) elevated pH values likely due to the polymerization of H_4SiO_4 which generally occurs under warm and/or arid climate conditions (Eugster 1980);

and/or, (2) solute concentration fluctuations (Hesse 1989) usually occurring as a result of an influx of waters interacting with a silica-rich host material. Periodic influx of 'flood' waters is consistent with intermittent, intraformational breccia beds that were observed in the middle member of the SMF interspersed between laminar chert beds. In thin section, laminae overlying silica nodules are occasionally disrupted by fine cracks (Fig. 6) which could be interpreted to result from dehydration of gel-like deposits (Iler 1979). Conspicuous colloform and isopachous vug fill fabrics indicate fluctuating precipitation phases likely resulting from alternating hydrologic fluxes which arguably could be initiated by percolation of meteoric waters in contact with silica-rich host material. The micromorphological silica features suggest that the SMF cherts may have precipitated in response to fluctuating pH and cation concentrations induced by a periodic influx of meteoric water, typically associated with either shallow continental lakes or groundwater. In toto, the petrographic observations indicate that the chert has not been significantly altered by metamorphic processes that would have resulted in recrystallization of silica to mega quartz and the loss and destruction of radial and fibrous micromorphological silica fabrics.

Warm crystallization temperatures in the range of 27–33 °C were inferred from oxygen and hydrogen isotope values of SMF chert nodule and silica precipitates. The inferred quartz crystallization temperatures of the SMF chert are incompatible with the hypothesized, cold temperature extremes of −50 °C (Kirschvink 1992) of the proposed, catastrophic "snowball" Earth glacial episodes (which includes the Sturtian Ice Age). However, it has been argued that marine diamictites (interpreted as tillites by some researchers) were principally emplaced during the final meltdown stage of "snowball" Earth events (e.g., Caldiera and Kasting 1992; Hoffman and Schrag 2002; Evans and Raub 2011 and references therein). Kirschvink (1992) and Hoffman et al. (1998) suggested that volcanic eruptions and degassing increased carbon dioxide levels in Earth's atmosphere which: (1) led to global "greenhouse" conditions following "snowball" Earth glacial events; and, (2) produced post-glacial, global surface temperatures of ~50 °C during the final meltdown stage. Eyles and Januszczak (2004) have argued that the Neoproterozoic glaciation(s) were likely regional in scope and no more severe than other glaciations recorded in Earth history. Further, they suggest that many of the marine diamictites are not tillites and can be explained by deposition in evolving tectonically-active rift basins. The reader is referred to several review and research articles pertaining to the on-going discussion of Neoproterozoic glaciation and the contradictory models (Allen and Etienne 2008; Zheng-Xiang et al. 2013; Evans and Raub 2011; Delpomdor et al. 2016 and references therein). If indeed global Earth temperatures rebounded to ~50 °C during the putative late stages of "snowball" Earth meltdown events, it remains a possibility that chert in the post 742 Ma SMF could have formed under elevated temperatures at—or near, the conclusion of the Sturtian Ice Age (~750 Ma; Corsetti et al. 2003). Relative to the marine diamictites that accumulated during late stage "snowball" Earth meltdown events, the bedded chert in the SMF were deposited in strikingly different depositional environments. Chert in the SMF likely formed in a shallow, non-marine depositional environment as opposed to the marine environments that typify "snowball" Earth diamictites. Additional lines of reasoning which suggest that chert in the SMF likely did not form in a late stage "snowball" Earth meltdown event, include: (1) an absence of facetted and striated clasts and other diagnostic glaciogenic features; and, (2) geochemical evidence that indicates that the relatively small (<10 cm diameter) angular, chert clasts of the upper breccia were locally derived from underlying laminar chert beds of the SMF and not from far-travelled extrabasinal clast assemblages typical of "snowball" Earth diamictites. The SMF represents a notable change from a marine depositional environment to a continental/terrestrial depositional environment. An unconformity of unknown duration separates the SMF from the marine sedimentation cycles of the stratigraphically older Neoproterozoic Chuar Group which were most likely driven by glacio-eustasy (Dehler et al. 2001). Collectively, there appears to be sufficient evidence to tentatively and cautiously conclude that chert in the SMF likely formed sometime after the Sturtian Ice Age. Additional research is needed to conclusively determine if the continental, small-scale, intraformational chert breccias of SMF (AZ) are temporally correlative with the larger-scale diamictites (tillites) of the Kingston Peak Formation (CA), as inferred by the studies of Young et al. (1981) and Link et al. (1993).

5 Summary and conclusions

1. The middle and upper members of the Sixtymile Formation in eastern GCNP contain chert suitable for palaeotemperature analysis inferred from oxygen and hydrogen isotope measurements, confirmed by petrographic observations and stable isotopic data.
2. Application of the Knauth and Epstein (1976) method for assigning palaeotemperatures to isotopic values of chert yield a long-term palaeotemperature range of 27–33 °C for the Sixtymile Formation. Accuracy of these palaeotemperature estimates is subject to certain assumptions inherent in the interpretation of isotopic data.

3. The oxygen and hydrogen isotope values indicate that meteoric (non-marine) waters were present during chert crystallization.
4. Field evidence in conjunction with oxygen and hydrogen isotope values of chert from the Sixtymile Formation tentatively suggest that chert in the Sixtymile Formation likely did not precipitate during a putative final meltdown stage of "snowball" Earth events.

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Conflict of interest As sole author, the corresponding author states that there is no conflict of interest.

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