Heat treatment of Kalahari and Cape silcretes: impacts upon silcrete chemistry and implications for geochemical provenancing

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Abstract

Recent studies in southern Africa and eastern Australia have demonstrated the feasibility of using a geochemical fingerprinting approach to determine the source locations from which silcrete raw materials were procured prior to their use in stone tool manufacture. The impact of intentional heat treatment of silcrete upon its chemistry, however, is unknown, meaning that heat-treated silcrete artefacts have to date been excluded from provenancing studies. This investigation presents the first high-resolution experimental analysis of the impacts of heat treatment upon the chemical composition of silcrete. The study compares the composition of unheated control samples against samples heat-treated to target temperatures of up to 600°C taken from four silcrete blocks from South Africa and Botswana. Chemical compositions of samples are determined using ICP-MS and ICP-AES. Experimental results indicate that heat treatment has a limited impact upon silcrete chemistry. Only 7 out of 65 minor, trace and rare earth elements analysed (Al_2O_3, Fe_2O_3, K_2O, As, Cr, Cs and Cu) were depleted beyond expected error limits following controlled heating. There was no consistent pattern of elemental depletion across the four silcrete samples, although a greater number of elements were depleted from chalcedony-cemented Kalahari silcretes compared to microquartz-cemented Cape silcretes. We conclude that it is safe to use chemical data from heat-treated artefacts from the Cape as part of geochemical fingerprinting studies; however, we recommend that Cu and Cs concentrations be omitted from any statistical analyses until the effects of heat treatment upon these elements are fully understood. We echo the conclusions of previous studies by recommending that chalcedony-cemented silcrete artefacts that show signs of burning or intentional heat treatment be excluded from provenancing studies in the Kalahari and potentially elsewhere.

Key words

Heat treatment; silcrete; Kalahari; Cape coastal zone; geochemistry

1. Introduction

Silcrete is a highly indurated but physically and chemically variable archaeological raw material consisting of strongly silicified sediment, soil, regolith or bedrock (Milnes and Thiry, 1992; Nash and Ullyott, 2007; Thiry and Milnes, 2017). Owing to its knapping qualities, silcrete was widely used for stone tool manufacture in various parts of Africa, Asia, Australia, Europe and the Americas (see Wragg Sykes and Will, 2017, for examples of recent studies). Unlike other siliceous rock types (e.g. flint, chert, quartz and quartzite) that were formed at depth, exhumed and advantageously exposed at the surface prior to their exploitation for tool-making, silcretes develop in near-surface environments and hence are explicitly linked to the landscapes in which prehistoric peoples gathered resources (cf. Thiry and Milnes, 2017).

Recent investigations in southern Africa and eastern Australia have demonstrated that, using a geochemical fingerprinting approach, it is possible to determine the source locations from which silcrete raw materials were procured prior to their use in stone tool manufacture. In the Kalahari Desert of Botswana, Nash et al. (2013a) demonstrated that the peoples who occupied White Paintings Shelter in the Tsodilo Hills during the Middle Stone Age (MSA) routinely transported silcrete for tool production over distances of up to 295 km. Building upon this study, Nash et al. (2016) established that the users of three other MSA sites in northwest Botswana procured at least some of their silcrete from similar locations. In the Arcadia Valley of eastern Australia, Cochrane et al. (2017) further showed that it is possible to use silcrete chemistry to identify specific creeks where cobbles were procured for the manufacture of a variety of tools.

In light of these studies, it should now be feasible to employ geochemical analyses of silcrete lithics to determine spatio-temporal patterns of raw material transport, and hence human mobility, in regions of the world with chronologically well-constrained Stone Age sites and where silcrete was widely used for tool production. A promising area for such studies is the Western and Eastern Cape coastal zone of South Africa (hereafter referred to as the Cape). Geochemical fingerprinting has yet to be tested at any of the internationally important Stone Age sites in this region, despite considerable potential at silcrete-rich assemblages including Blombos Cave (Henshilwood et al., 2001), Pinnacle Point (Marean, 2010), Klasies River (Singer and Wymer, 1982) and Diepkloof (Porraz et al., 2013b). Nash et al. (2013b) have, however, demonstrated that silcretes across the Cape show significant chemical variability, to the extent that individual raw material acquisition sites should be distinguishable from their geochemical signature.

A potential barrier to the use of geochemical fingerprinting on South African silcretes is the uncertain impact of heat treatment upon silcrete chemistry. Heat treatment was a transformative technology widely used by our human ancestors during the MSA and Later Stone Age (LSA) to improve the flaking qualities of silcrete (e.g. Brown et al., 2009; Brown et al., 2012; Henshilwood, 2012; Wadley, 2013; Wurz, 2013; Wadley and Prinsloo, 2014). Published evidence of silcrete heat treatment is now available from several archaeological sites across the Cape (e.g. Brown et al., 2009; Mourre et al., 2010; Schmidt et al., 2015; Delagnes et al., 2016; Porraz et al., 2016; Schmidt and Mackay, 2016; Schmidt and Hogberg, 2018). Heat treatment acts to transform silcrete by causing a loss of chemically bound ‘water’ from the rock structure, which, in turn, leads to the formation of new Si-O-Si bonds (Schmidt et al., 2017a; Schmidt et al., 2018). An unwanted side effect (from the perspective of geochemical fingerprinting) is the chemical synthesis of molecular water, which is evacuated as high pressure steam (Schmidt et al., 2012; Schmidt, 2014) and may mobilise some chemical elements. For this reason, Nash et al. (2013a) and Nash et al.

(2016) avoided the analysis of silcrete samples that showed any sign of having been heat-altered or burnt in their study of MSA artefacts from the Kalahari.

The aim of this study is to document the results of the first high-resolution controlled experimental investigation into the impacts of heat treatment on the chemical composition of silcrete. The study builds upon work by Schmidt et al. (2017b), who described the crystallographic and 'water'-related processes taking place upon heat treatment during the same experiment. Schmidt et al. also identified a previously undescribed mechanism – steam leaching – to explain the depletion of a small number of chemical elements during heat treatment. Here, we report the full chemical dataset from our experiment. Having described the limited chemical transformations arising from heat treatment, we explore the implications of our results for the use of silcrete in archaeological provenancing studies.

2. Materials and methods

The experimental method used in this study was designed to provide details of the chemical changes associated with the heat-treatment of silcrete across a range of potential treatment temperatures. This necessitated the high-resolution characterisation of changes in a limited number of representative samples, as opposed to using a larger set of samples where intra-sample heterogeneity could not easily be assumed or controlled.

2.1 Sample characteristics

The experiment utilised two samples of silcrete from North-West Province, Botswana, and two from Western Cape Province, South Africa (Table 1). Sampling sites were chosen on the basis that either (in the case of the Western Cape samples) the selected outcrops were known to have been used by MSA/LSA peoples for raw material procurement (Porraz et al., 2013a; Schmidt et al., 2015; Porraz et al., 2016), or (for the Kalahari samples) were part of a larger area where silcrete is known to have been acquired during the MSA (Nash et al., 2013a; Nash et al., 2016). Samples from Botswana were collected in primary position from two outcrop areas close to Samedupi Drift on the Boteti River; those from the Western Cape were collected in primary position from two weathering profiles near the towns of Hopefield and Redelinghuys (Figure 1). Each sample silcrete block was ~20 cm in diameter.

Table 1: Silcrete block sample numbers, locations and properties (data from Schmidt et al., 2017).

Sample	Location	Petrography, porosity and 'water' content
BW-14-01	Samedupi Drift, Boteti River, North-West District, Botswana	Well-sorted drainage-line silcrete with GS-fabric. Clasts: ~80 vol% with average size ~0.25 mm. Cement: epitaxial length-slow (LS-) chalcedony overgrowth on clasts, void filling length-fast (LF-) chalcedony. Porosity 0.83 vol%. H_2O+SiOH 0.89 wt%.
BW-14-02	Samedupi Drift, as above	Well-sorted drainage-line silcrete with GS-fabric, as above. Porosity 0.41 vol%. H_2O+SiOH 0.54 wt%.
WK-13-13	Near Redelinghuys, Western Cape, South Africa	Very poorly sorted pedogenic silcrete, with grain-supported (GS-) to floating (F-) fabric. Clasts: ~70 vol% with average size ~0.92 mm. Cement: microquartz with crystal size of <5 µm. Porosity 2.55 vol%. H_2O+SiOH 0.56 wt%.
WK-15-01	Near Hopefield, Western Cape, South Africa	Very poorly sorted pedogenic silcrete, with F-fabric. Clasts: 30±40 vol% with average size ~0.2 mm. Cement: microquartz with crystal size of ~15 µm. Porosity 1.69 vol%. H_2O+SiOH 0.36 wt%.

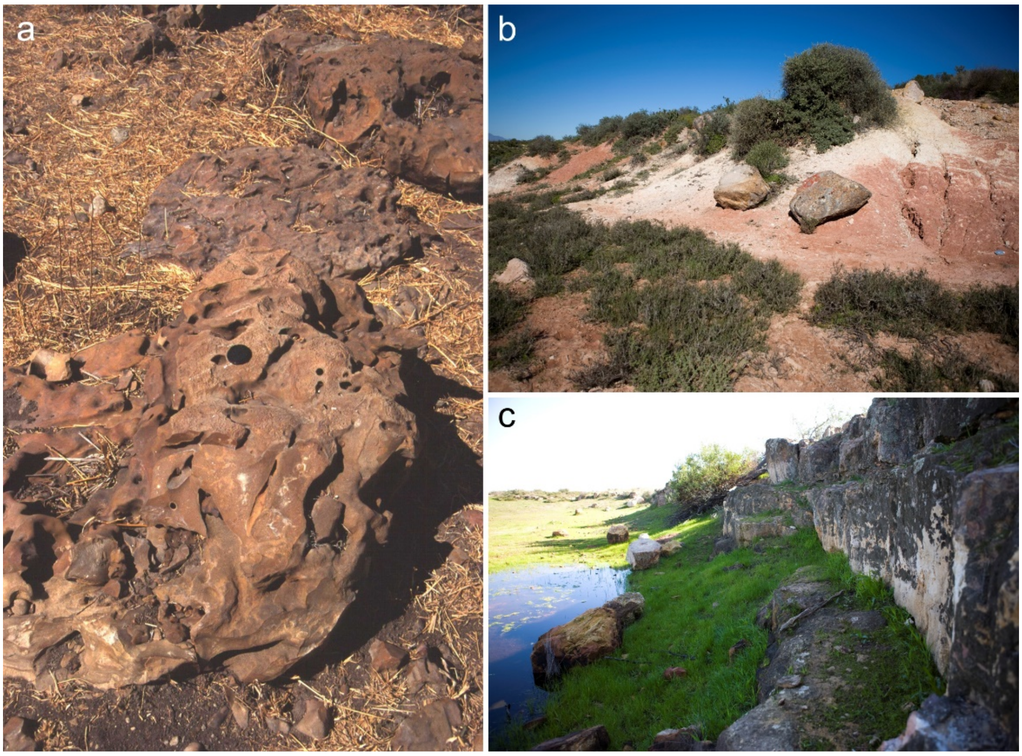

Figure 1: Silcrete sampling areas. a) Samedupi Drift, Boteti River, North-West District, Botswana (samples BW-14-01 and BW-14-02); b) near Redelinghuys, Western Cape, South Africa (sample WK-13-13); and c) near Hopefield, Western Cape, South Africa (sample WK-15-01).

The petrological characteristics of each silcrete sample (originally reported in Schmidt et al., 2017) are summarised in Table 1. The two samples from Botswana have a grain-supported (GS)-fabric (using the terminology of Summerfield, 1983a) consisting of rounded well-sorted clasts in a matrix of chalcedony. Both exhibit diagnostic characteristics of drainage-line silcrete, a variant of groundwater silcrete (see Nash and Ullyott, 2007; Ullyott and Nash, 2016). The matrix in each sample comprises layered epitaxial length-slow chalcedony overgrowths of variable thickness on clasts, with larger voids filled with length-fast chalcedony. The matrix in both samples is transparent in unpolarised light, suggesting a low concentration of non-quartz impurities. Porosity (vol%) and 'water' content (wt% H_2O+SiOH) are both higher for sample BW-14-01 compared to sample BW-14-02. BW-14-01 has the lowest pore space relative to its 'water' content of the four samples (water and por-space measurements followed the protocol proposed by: Schmidt et al., 2011; Schmidt et al., 2017a).

The South African samples both comprise angular, very poorly sorted quartz clasts in a microquartz matrix. Sample WK-13-13 has a floating (F-) to GS-fabric (sensu Summerfield, 1983a), while sample WK-15-01 has an F-fabric. The matrix in WK-13-13 is almost opaque in unpolarised light, revealing higher concentrations of non-quartz components than in WK-15-01. Both samples exhibit characteristics diagnostic of pedogenic silcrete (see Nash and Ullyott, 2007; Ullyott and Nash, 2016). Porosity and 'water' content are both higher for sample WK-13-13. None of the Botswana and Cape samples contain significant amounts of hydrous minerals such as goethite.

2.2 Sample preparation and analysis

Sample preparation followed a protocol designed to minimise within-sample heterogeneity and ensure that the chemical stability of samples subject to various stages of heat treatment could be compared. For this, nine cubes with an average edge length of ~3 cm, volume of ~27 cm^3 and weight of ~70 g were cut from each of the four original silcrete blocks (Figure 2a,b). Each cube was cut in half (Figure 2c) and mechanically crushed, with the two crushed half-cubes then homogenised and sieved to produce subsamples (referred to here as ‘granulars’) comprising silcrete fragments between 3 and 15 mm (Figure 2d). The step of mixing and homogenisation was intended to provide uniform granulars from each cube, although heterogeneity of the minor and trace element concentration within a single cube cannot be completely ruled out. This protocol cannot control for heterogeneities in trace element concentration across the whole initial block (Figure 2a), but was adopted such that both infrared spectroscopic and trace element data could be obtained. The results of infrared analyses are published elsewhere (Schmidt et al., 2017b). To address the remaining within-sample heterogeneity, we adapted the expected error bars accordingly (see below). A relatively large fragment size for the granulars was chosen over finer powders, as the thermal transformations in larger fragments should be more comparable with those in the size range of silcrete waste flakes generated during stone tool manufacture.

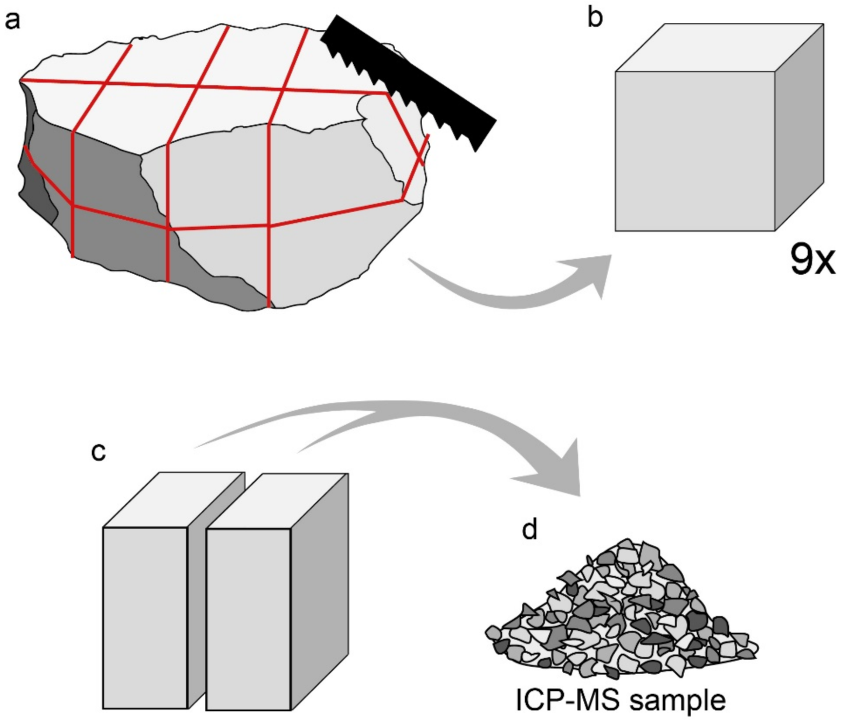

Figure 2: Protocol used for sample preparation.

Each of the 36 granulars was separated into two aliquots. One aliquot was used as a control without further experimental treatment; this was fine-crushed in an agate ball-mill (to 70% passing <2 mm or better), split using a rotary splitter and pulverised in an agate ball-mill (to 85% passing 75 µm or better). The resulting powder was analysed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively couple atomic emission spectroscopy (ICP-AES) to determine concentrations of 65 minor and trace elements. The other aliquot was heated (using an electrical laboratory furnace) to one of the following target temperatures – 110°C, 200°C, 250°C, 300°C, 350°C, 400°C, 450°C, 500°C and 600°C – and then fine-crushed, pulverised, and analysed. A heating rate of 4°C/min was used to avoid sample fracturing (after Schmidt et al., 2013; Schmidt et al., 2015), with the target temperature held for 2 hours to allow time for all ‘water’-related chemical transformations to be completed (Schmidt et al., 2016).

The following instrumentation was used for the analysis of both the control and heat-treated aliquots from each sample. Minor oxide and base metal concentrations were determined using a Varian 700 series ICP-AES instrument. Volatile, trace and rare earth element concentrations were determined using an Elan 9000 ICP-MS instrument. Minor elements are reported as oxides in wt% and trace elements in ppm. All analyses are certified under quality control certificates SV11196510 and SV12059240 issued by ALS Minerals, Seville, Spain. Full results of the chemical analysis of control and heat-treated samples are included in the Supplementary Dataset.

To determine change in chemical composition, element values for each heat-treated aliquot were subtracted from the values for its corresponding control aliquot. This ‘loss’-value was then subtracted from the mean concentration of the same element as averaged across the nine control aliquots from the respective silcrete block. The resulting values are representative of the overall concentration of each chemical element in a sample and display any change after heating to different temperatures.

3. Results

3.1 Presentation of data

The concentrations of minor, trace and rare earth elements at the various stages of heating are shown, by sample, in Figures 3-6 (Kalahari samples in the upper panels, Cape samples in the lower). Note that those elements that were initially at concentrations just above instrumental detection limits at the start of the experiment and that exhibited values that fluctuated above and below detection limits are not illustrated.

Values in each panel of Figures 3-6 are plotted with two error bars. The first (black) corresponds to the instrumental error for the respective element. For elements where the instrumental error range is extremely small (e.g. TiO_2, Ba, Cs, V) this error bar is not shown. The second (normally larger, grey) error bar corresponds to the range of element concentration values as recorded in the nine control granular aliquots from the same sample – this reflects the heterogeneity of the sample with respect to the plotted element. Only values for elements plotting below the lower range of the grey error bars for the aliquot heated to 110°C can confidently be considered as indicating element depletion.

3.2 Changes in minor element concentrations

The impact of experimental heat treatment on minor element concentrations differs between the silcrete samples from the Kalahari and Cape, with no consistent patterns identified across all four samples. For the Kalahari samples, concentrations of three minor elements are depleted after heat treatment (i.e. they plot below the expected error). Both Al_2O_3 and Fe_2O_3 are depleted in granulars from sample BW-14-01 heated to above 500°C (Figure 3a), with the depletion trend appearing in granulars heated to 200°C and above. K_2O is depleted in the two granulars from sample BW-14-02 heated to 400°C and 450°C only (Figure 3b). Other minor elements remained stable (i.e. within expected error limits) in these samples. Neither of the silcrete blocks from the Western Cape showed any depletion of minor elements over the course of the experiment, with concentrations either remaining stable or fluctuating within error limits (Figure 3c,d).

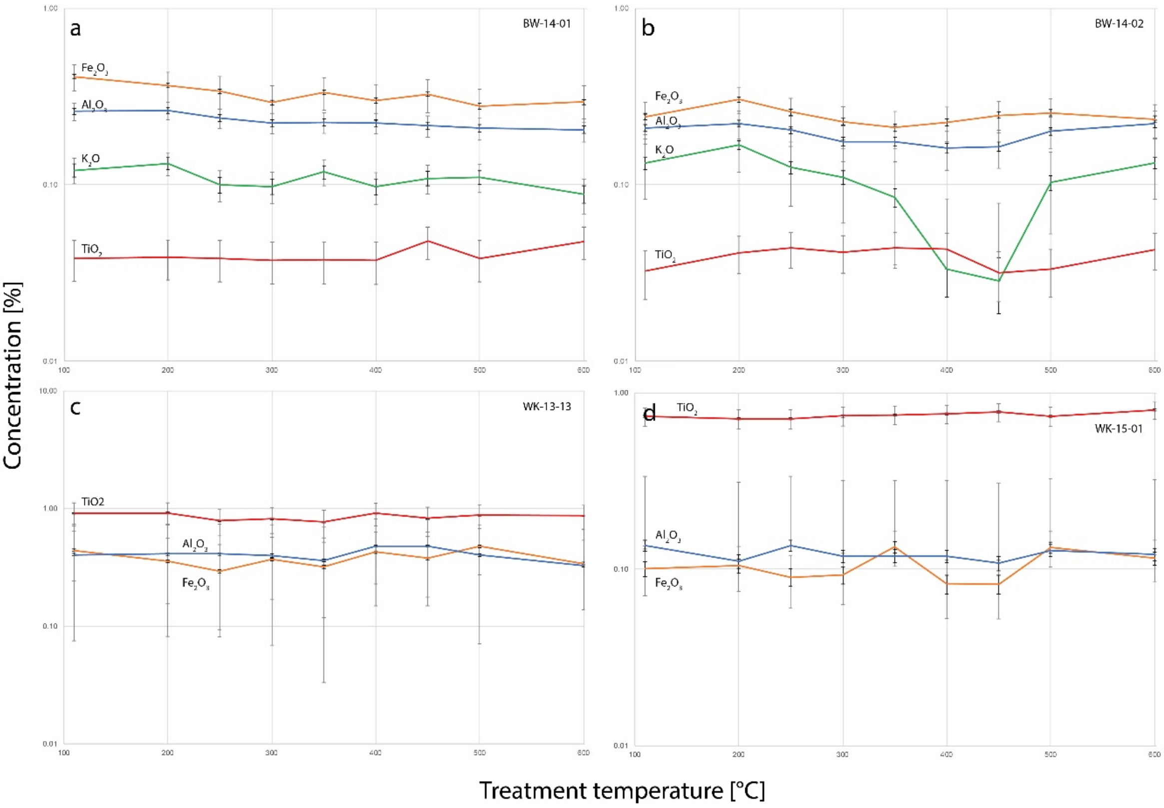

Figure 3: Plots of minor element concentrations in the four silcrete blocks (Al_2O_3, Fe_2O_3, TiO_2 for all samples, plus K_2O for the Kalahari samples). See text for details of error bars.

3.3 Changes in trace and rare earth element concentrations

The impact of experimental heat treatment on trace and rare earth element concentrations is limited, with evidence of depletion identified in only four of the elements analysed. For the trace elements, results again show no consistency between silcretes from the Kalahari and Cape. For the Kalahari samples, Cu, As and Cs are depleted in almost all heated granulars in BW-14-01 (Figure 4a); Cr is depleted in the same sample at 500°C (Figure 5a). However, despite having very similar petrological characteristics, sample BW-14-02 showed no evidence of trace element depletion (Figures 4b and 5b).

For the samples from the Cape, Cu is depleted in all granulars from sample WK-13-13 heated to above 350°C, while Cs is depleted in the two granulars from the same sample heated to above 500°C (Figure 4c). Sample WK-15-1 showed no evidence of trace element depletion (Figure 4d and 5d). Rare earth element concentrations remained relatively stable or fluctuated within error limits in all four samples (Figure 6), with no evidence of depletion.

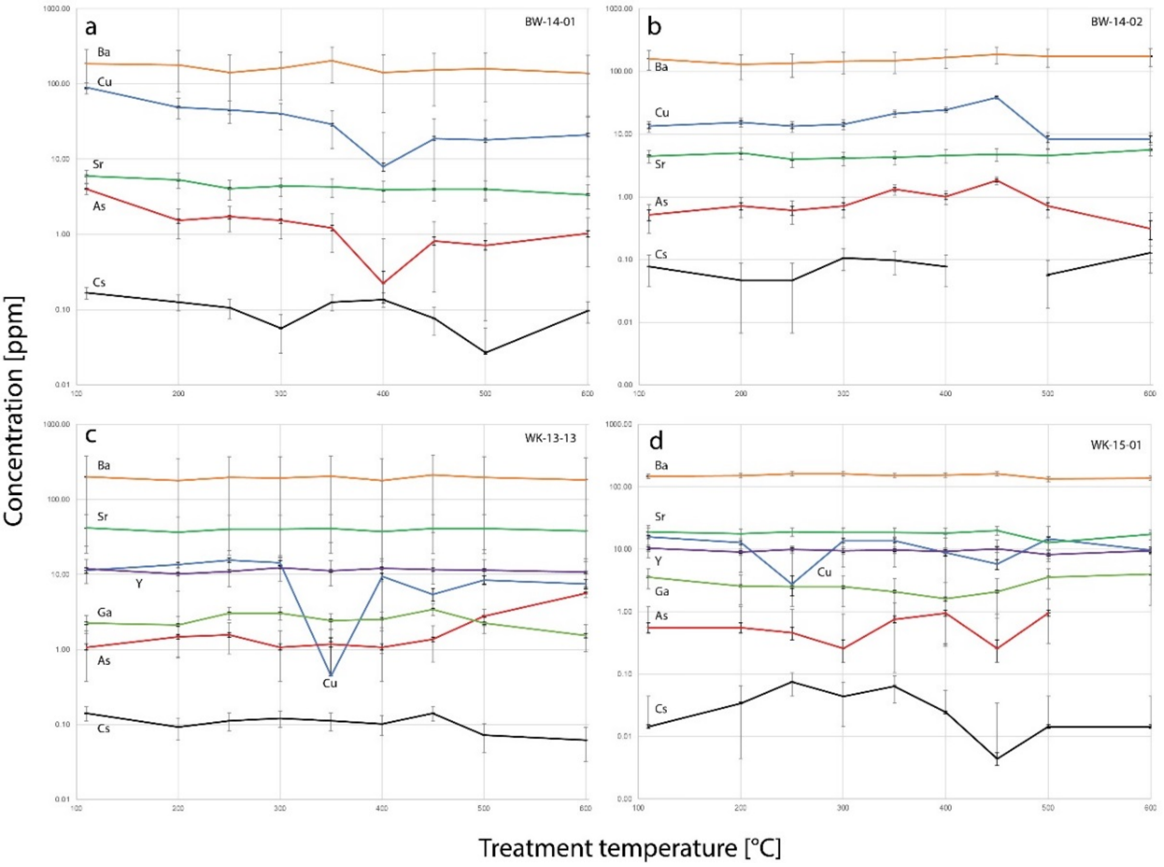

Figure 4: Plots of trace element concentrations in the four silcrete blocks (As, Ba, Cs, Cu, Sr for all samples, plus Ga, Y for Cape samples). See text for details of error bars.

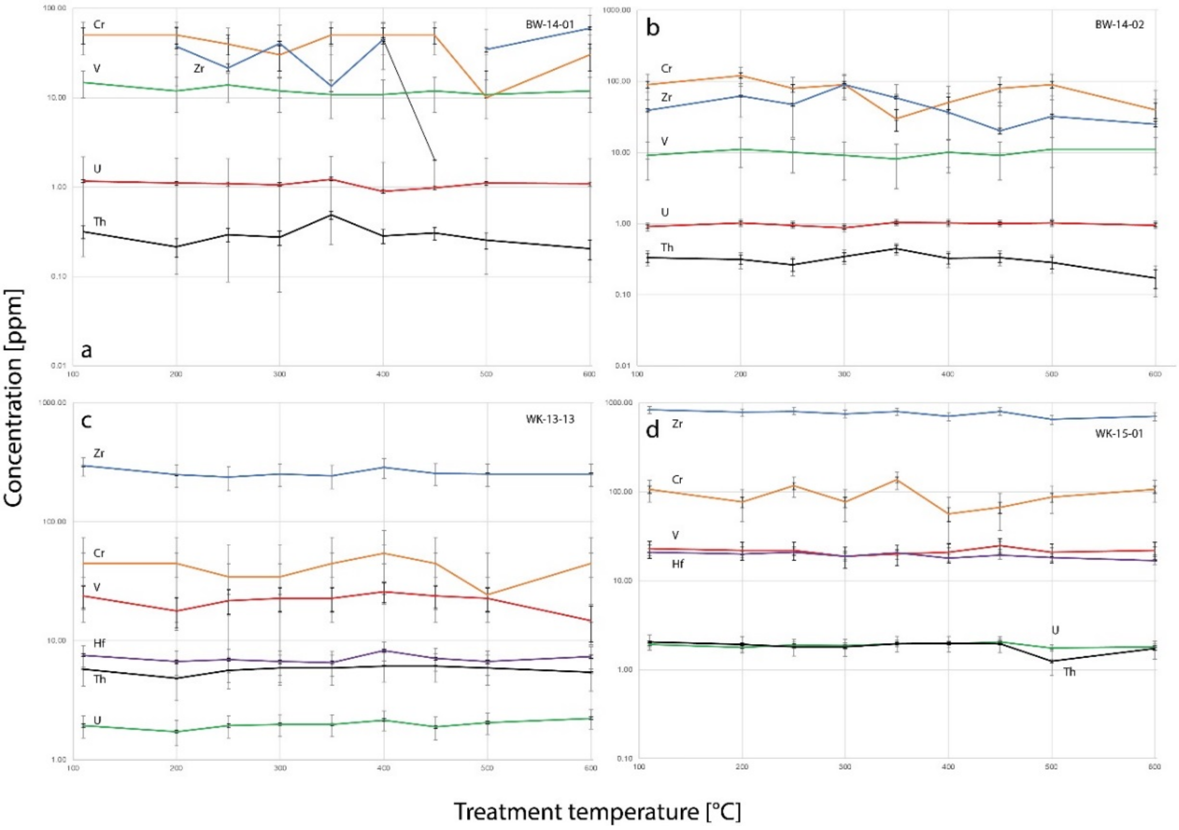

Figure 5: Plots of trace element concentrations in the four silcrete blocks, continued (Cr, Th, U, V, Zr for all samples, plus Hf for Cape samples). See text for details of error bars.

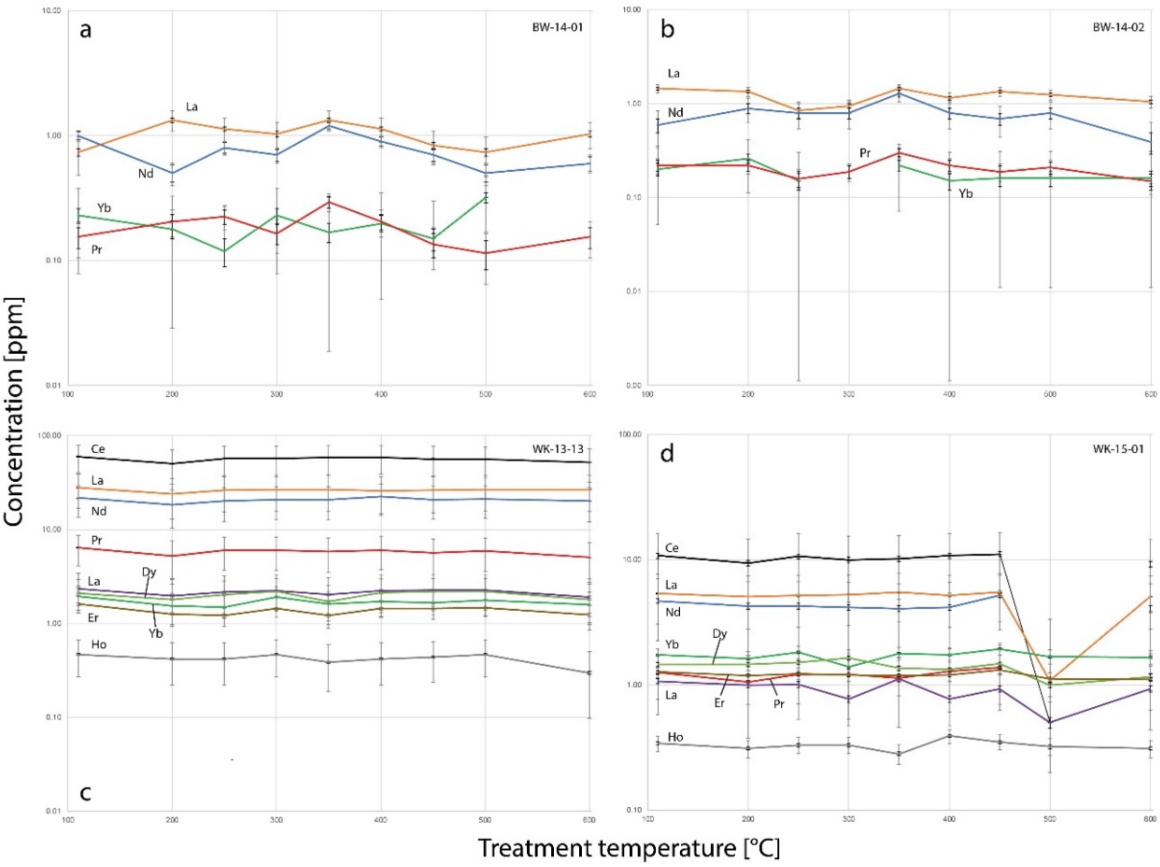

Figure 6: Plots of rare earth element concentrations in the four silcrete blocks (La, Nd, Pr, Yb for all samples, plus Ce, Dy, Er, Ho for Cape samples). See text for details of error bars.

4. Discussion

4.1 Mechanisms of element depletion

The results presented in section 3 suggest that – within the bounds of our experimental methods and relatively small number of samples – heat treatment causes limited chemical transformations within silcrete. Our data may be further influenced by weight loss due to water evaporation in the samples but these effects are insignificant with respect to the experimental error (in no case exceeding 0.8 wt%; see Schmidt et al., 2017b). A total of 7 of the 65 chemical elements analysed using ICP-MS and ICP-AES were depleted in at least one sample following heating, but none were depleted across all four samples. The greatest change occurred in the chalcedony-cemented Kalahari drainage-line silcretes, where Al_2O_3, Fe_2O_3, Cu, As, Cs and Cr were depleted in sample BW-14-01, but only K_2O in BW-14-02. The chemistry of the microquartz-cemented South African pedogenic silcretes remained largely unaffected by heat treatment, with only two elements (Cu, Cs) depleted as a result of heating (both in sample WK-13-13).

As Schmidt et al. (2017b) discuss, Cs and As are volatile elements and could be lost relatively easily during heating. Al_2O_3, Fe_2O_3, K_2O, Cu and Cr were likely depleted as a result of steam leaching. In the case of the Kalahari silcrete samples, which have lower pore space relative to their 'water' content (see Table 3), the steam generated during heating may have dissolved the cement surrounding pores, leading to the evacuation of selected elements. The impact of this effect was greatest in sample BW-14-01, which has the lowest pore space relative to its ‘water’ content of the four samples, potentially building up the highest steam pressure during heat treatment.

4.2 Implications for archaeological provenancing studies

Our experimental results suggest that the impact of heat treatment on the chemistry of silcrete samples from the Cape is sufficiently limited to permit the analysis of heat-treated silcrete artefacts in future geochemical provenancing studies. Only two silcrete blocks from the Western Cape were analysed in detail for this study. However, given that (i) the petrographic characteristics of these blocks are broadly consistent with other pedogenic silcretes from the Cape, and (ii) pedogenic silcrete is by far the dominant silcrete type across the coastal belt (see Summerfield, 1983b; Roberts, 2003) and hence most likely to have been used for stone tool manufacture, the results should be more widely applicable in archaeological investigations.

We recommend that data for Cs and Cu concentrations within samples be excluded from future provenancing studies until the impact of steam leaching on these elements is fully understood. This recommendation is made on the basis of statistical analyses of ICP-MS and ICP-AES data for 50 silcrete samples taken from 12 outcrops spread across the Cape coastal belt from Lutzville in the west to Grahamstown in the east. These data were originally presented as Supplementary Information in Nash et al. (2013b), and represent the largest published set of high-resolution geochemical data available for silcretes from the Cape.

Canonical discriminant analysis was performed first on data for all 65 chemical elements within the Cape silcrete dataset and then with Cs and Cu removed. As in the original study by Nash et al. (2013b), samples in both sets of statistical analyses were grouped by associated bedrock type. The discriminant plot in Figure 7 shows the first two functions arising from these analyses. Functions 1 and 2 explained 78.1% and 95.9% respectively of the cumulative variance in the ‘all elements’ analysis (solid symbols), and 68.6% and 95.4% in the reanalysis with Cs and Cu removed (open symbols). The main contributors to Function 1 in the ‘all elements’ analysis were TiO_2, Nb and Ce; for Function 2, Er, Eu, Gd and Nb were most significant. For the reanalysis, TiO_2, Ta and Dy were the main contributors to Function 1 and Ce, Eu and Gd to Function 2. The results show that, while the position of some samples on the discriminant plot shift slightly between analyses, the distinct clustering of silcretes according to bedrock lithology remains unchanged – in short, removing Cs and Cu has little or no impact on statistical discrimination between the groups of samples.

The impact of heat treatment on the chemistry of Kalahari samples, while limited and variable, was greater than for the Cape samples and involved the depletion of three minor elements. Our second recommendation therefore is to reaffirm that silcrete artefacts from the Kalahari that show any sign of heat alteration or burning should be excluded from geochemical fingerprinting studies. Whether this caution need be extended to all chalcedony-cemented silcretes requires further experimental verification. We note, however, that chalcedony-cemented rocks, in general, are more susceptible to steam leaching (cf. Pelto, 1956). Inspection of silcrete samples in thin-section is recommended to determine the dominant cement type(s) present and the environment/mode of silcrete formation (i.e. pedogenic, groundwater, drainage-line or lacustrine/pan; see Nash and Ullyott, 2007) prior to undertaking geochemical analyses. Echoing Schmidt et al. (2017b), despite having the same geological ‘name’, silcretes formed in different contexts and with different silica cements undergo quite different chemical transformations when heat treated.

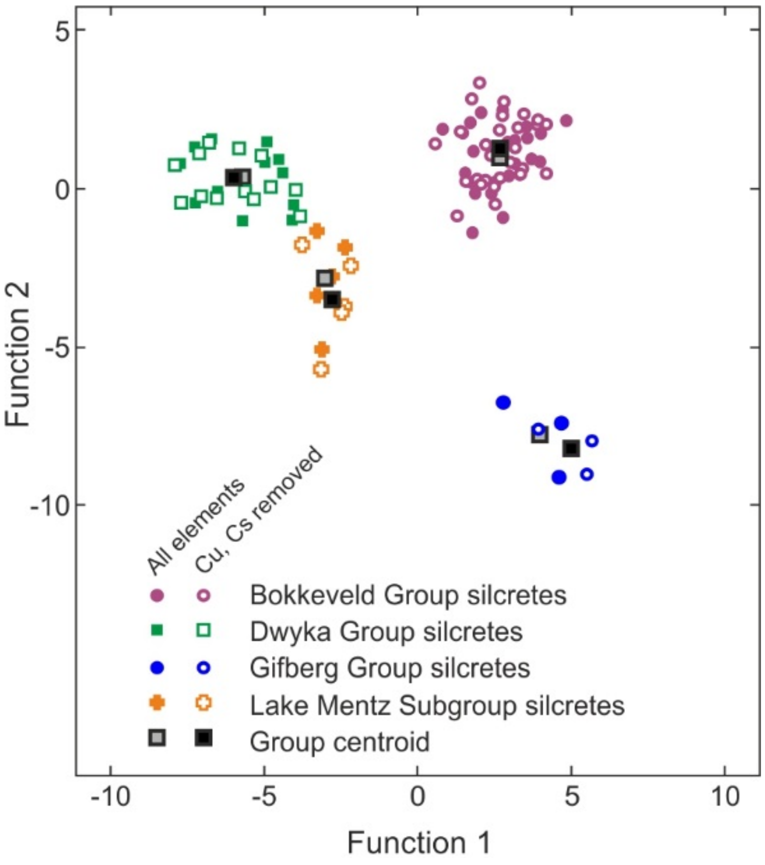

Figure 7: Results of canonical discriminant analysis of chemical data for 50 silcrete samples from across the Cape coastal belt, South Africa, grouped by associated bedrock type (see Nash et al., 2013b, for further details and original dataset).

5. Conclusions

The aim of this study was to document the results of an experimental investigation into the impacts of heat treatment on the chemical composition of silcrete. We identify that heat treatment has a limited impact upon silcrete chemistry, with only 7 out of 65 minor, trace and rare earth elements analysed being depleted following controlled heating. Of these, Al_2O_3, Fe_2O_3, K_2O, Cu and Cr were probably depleted via the process of steam leaching, while the volatiles Cs and As were burned off during heating. Significantly, there was no consistent pattern of elemental depletion across silcrete samples from the Kalahari and Cape, with the degree of depletion most likely linked to the total pore space within a silcrete relative to its ‘water’ content. We conclude that, within the limits of our experiment, it is safe to use chemical data for heat-treated artefacts from the Cape as part of geochemical fingerprinting studies, but recommend that Cu and Cs concentrations be omitted from any statistical analyses. We repeat the conclusions of previous studies by suggesting that any chalcedony-cemented silcrete artefacts from the Kalahari (and potentially elsewhere) that show signs of burning or intentional heat treatment be excluded from provenancing studies.

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