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Tempering-residue on heat-treated silcrete: an experimental perspective and a potential analytical protocol

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ABSTRACT

Silcrete heat treatment in the South African Middle Stone Age has been understood as a proxy for several key concepts in the evolution of early anatomically modern humans, although relatively little is yet known about the techniques and procedures used for it. Tempering-residue on heat-treated artefacts is one of the few known proxies for such a heating technique. It was reported to indicate heat treatment in open-air fires rather than in a sand-bath. There are however, several questions that need to be answered before tempering-residue can be used as an unambiguous proxy for heat treatment in open-air fires. These questions included: does it exclusively form in contact with embers? Is it only produced by green wood? We investigate the conditions under which tempering-residue forms using an experimental approach and wood from the zone of natural silcrete occurrence in South Africa. Our results confirm earlier publications by highlighting that tempering-residue only forms during heat treatment in direct contact with embers. Moreover, it indicates the use of green (not dried) wood in these fires. We also propose a potentially non-destructive analysis protocol for identifying tempering-residue on silcrete artefacts using infrared and Raman spectroscopy. The implications of these results for our understanding of early stone heat treatment and Middle Stone Age archaeology in general are highlighted by the ongoing debate about technical complexity, required investment and modern behaviours of early *Homo sapiens*.

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1. Introduction

Controlled heat treatment to improve the quality of silcrete for tool knapping has so far been documented from a handful of sites dating to the second half of the southern African Middle Stone Age (MSA) (Brown et al. 2009, Schmidt et al. 2015a, Porraz et al. 2013, Moure et al. 2010, Schmidt and Mackay 2016). In this context it has been understood as a proxy for complex cognition (Wadley 2013), sophisticated technical skills (Brown et al. 2009) and the willingness to spend large quantities of resources on tool production (Brown and Marean 2010). To work on these concepts, it is crucial to understand the techniques and procedures used for heat treatment and to apprehend how much investment in time, resources and labour was necessary for them. To investigate the conditions South African silcrete requires and, consequently, which techniques are necessary for its heat treatment, a first mineralogical analysis of the thermal transformations taking place during heating was conducted (Schmidt et al. 2013). The authors proposed that silcrete could potentially have been heat-treated in the embers of

open-air domestic fires, not demanding for large investments in time or resources. The first direct archaeological evidence for such a heating technique was presented by Schmidt et al., (2015a) who worked on the ca. 65–77 ka old Intermediate Howiesons Poort of Diepkloof Rock Shelter (Porraz et al. 2013, Tribolo et al. 2013). They found that a small number of all heat-treated silcrete artefacts contained a previously unrecognised residue: an organic wood tar produced by the distillation of plant exudations. This residue was reported to adhere to surfaces associated with the initial outer limits of the silcrete pieces during their heat treatment, indicating that the pieces were in contact with the glowing embers of an open-air fire while heated. Since this initial discovery, the MSA site of Mertenhof Shelter has yielded further indications of possible tempering-residue (Schmidt and Mackay 2016) although no analytical procedure has as yet confirmed its identity.

The concept of heat treatment in the embers of open-air fires is, however, not widely accepted in the context of the South African MSA. An alternative model, argued for by some authors (Brown et al. 2009, Wadley and Prinsloo 2014), is heat treatment in a sand-bath. Sand-bath heating relies on burying a piece of silcrete in sediment, over which a specially dedicated fire is lit (Schmidt 2016). The technique requires a higher investment in time and resources than heating in embers (Schmidt et al. 2015b). The implications of such a ‘high-

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investment model' for our understanding of the resource management of MSA hunter-gatherers (Brown and Marean 2010), the lithic *chaîne opératoire* and the technical complexity of early heat treatment (for the concept of technical complexity see for example Bettinger and Eerkens (1997)) are important. Thus, when studying silcrete heat treatment in the MSA, it is imperative to rely on unambiguous archaeological proxies that allow us to distinguish between heat treatment in open-air fires and more time-consuming techniques such as sand-bath heating. If tempering-residue is to be used as such a proxy, several questions arise:

- [1]. Under which conditions does tempering-residue form? Is it a phenomenon strictly associated with heat treatment in embers or is it also produced during sand-bath heating?
- [2]. Is sufficient moisture of the burned wood a condition for the formation of tempering-residue? If so, can tempering-residue be a proxy for the use of fresh/green wood instead of well dried wood in the tempering fire? This would also indicate that dead pieces of plant material accidentally buried along with silcrete during sand-bath heating do not produce tempering residue.
- [3]. Is tempering-residue on heated silcrete restricted to a small portion of the silcrete's outer surface or is silcrete normally completely enveloped by residue (i.e. what is the percentage of the silcrete's surface affected by the residue)?
- [4]. Is it possible to identify tempering-residue and distinguish it from other black residues potentially found on silcrete artefacts, using non-destructive analytical techniques?

To answer these questions we conducted heat treatment experiments with green and well-dried wood, using different heating techniques, and analysed the resulting tempering-residue by potentially non-destructive infrared and Raman spectroscopy. The heating techniques we explored include (1) burying the silcrete in a sand-bath under the fire, (2) placing a piece of silcrete alongside the fire and scraping glowing embers over it and (3) pushing a silcrete piece into the embers in the centre of the fire.

2. Materials and methods

2.1. Heating experiments

2.1.1. Raw materials for the experiments

We cut 30 kilograms of wood from *Searsia laevis* (L.) F.A. Barkley var. *villosa* (L.f.) Moffett, a resin producing species endemic to South Africa's Cape coastal zone where silcrete crops out (Mucina and Rutherford 2006, Summerfield 1983). Half of the wood (15 kg) was directly cut from a living *S. laevis* tree (green wood) and the other half was broken off from a part of the same tree that had died and dried in the sun (dry wood). We estimated the moisture content of green and dry wood by first weighing 5 pieces of each category (approx. 4 cm long and 2 cm in diameter) before drying for 48 hours at 70°C and

reweighing to determine the lost mass (Poorter et al. 2006). Volume was determined though immersion in water after weighing (Poorter et al. 2006). These measurements enable the determination of the mass of moisture lost per cubic centimetre of wood, a measure proportional to the wood's real moisture content. Green wood lost on average 4.5 times more weight than dry wood, indicating a significant difference between the moisture contents of each (Table 1). We heat-treated several pieces of silcrete with this wood. All pieces were flaked off a single block of grey silcrete with a red weathering rind, sampled in secondary position at location WK-13-08 of Schmidt et al. (2015a).

2.1.2. Experimental setup

We collected two sandbags of sandy sediment in front of the MSA site of Diepkloof Rock Shelter, and filled a ~20 cm deep and ~40x40 cm wide hole with this sediment (Supplementary Fig. 1). Dead pieces of wood, leaves, and grass lying on the ground around Diepkloof were deliberately collected along with and intermixed with the sediment to maintain a realistic heating ground that would contain organic matter. We made two fires using 15 kg of *S. laevis* on two separate wind still days, the first from green wood one day after collection and the second two days later from the dry wood. Using these fires we tested three different heating techniques or conditions: (1) Sand-bath heat treatment: a piece of silcrete (715 g/272 cm³ for the green wood experiment and 1065 g/404 cm³ for the dry wood experiment) was buried 2.5 cm below the surface. We placed a thermocouple on top and at the bottom of each piece to monitor temperature evolution during the experiments (Fig. 1a, Supplementary Fig. 1). The fires were then lit on top of the sediment, directly above the spot where the silcrete was buried. After lighting the fires we waited until sufficient embers formed to begin the above ground heating experiments. (2) Heat treatment beside the fires: a piece of silcrete (801 g/304 cm³ for the green wood experiment and 767 g/291 cm³ for the dry wood experiment) was placed beside the fire with a thermocouple under it during both experiments and embers were scraped on top of the pieces. These were then left untouched until the embers had transformed to a fine white ash that had cooled down to room temperature. (3) Direct heat treatment in the fires: a piece of silcrete (304 g/115 cm³ for the green wood experiment and 606 g/230 cm³ for the dry wood experiment) was pushed into the ash and ember cone at the base of each fire. No continuous temperature recording was made for the two silcrete pieces heat-treated in this way because it appeared impossible to measure the actual temperature evolution of the silcrete, and not the maximum temperature in the heating environment, with our experimental setup. However, we sporadically recorded the maximum temperature in the ash and embers cone of the fires during the treatment. To better monitor the possible formation of tempering-residue during the experiments we placed an additional 10 control flakes of silcrete (average size of ~4x4 cm) randomly distributed over the ash and ember cones of each fire. The experimental setup and some of the photos taken during the two burning experiments are shown in Figure 1.

Table 1
Results of the moisture content measurements of *S. laevis* wood used for the heating experiments

	Sample	Volume [cm ³]	Initial mass [g]	Density [kg/m ³]	Mass after 24h at 70°C [g]	Lost mass [g]	Lost mass [%]	Lost H ₂ O per cm ³ [g/cm ³]
Green wood	1	6	7.5916	1265.3	5.5335	2.0581	27	0.343
	2	3	3.3899	1130.0	2.3916	0.9983	29	0.333
	3	6	8.2385	1373.1	6.0081	2.2304	27	0.372
	4	4	4.7018	1175.5	3.3833	1.3185	28	0.330
	5	3	3.9936	1331.2	2.6964	1.2972	32	0.432
	6	8	5.8613	732.7	5.2669	0.5944	10	0.074
	7	5	3.9206	784.1	3.4652	0.4554	12	0.091
Dry wood	8	3	2.0067	668.9	1.7865	0.2202	11	0.073
	9	3	2.6119	870.6	2.3689	0.243	9	0.081
	10	6	4.4796	746.6	4.0759	0.4037	9	0.067

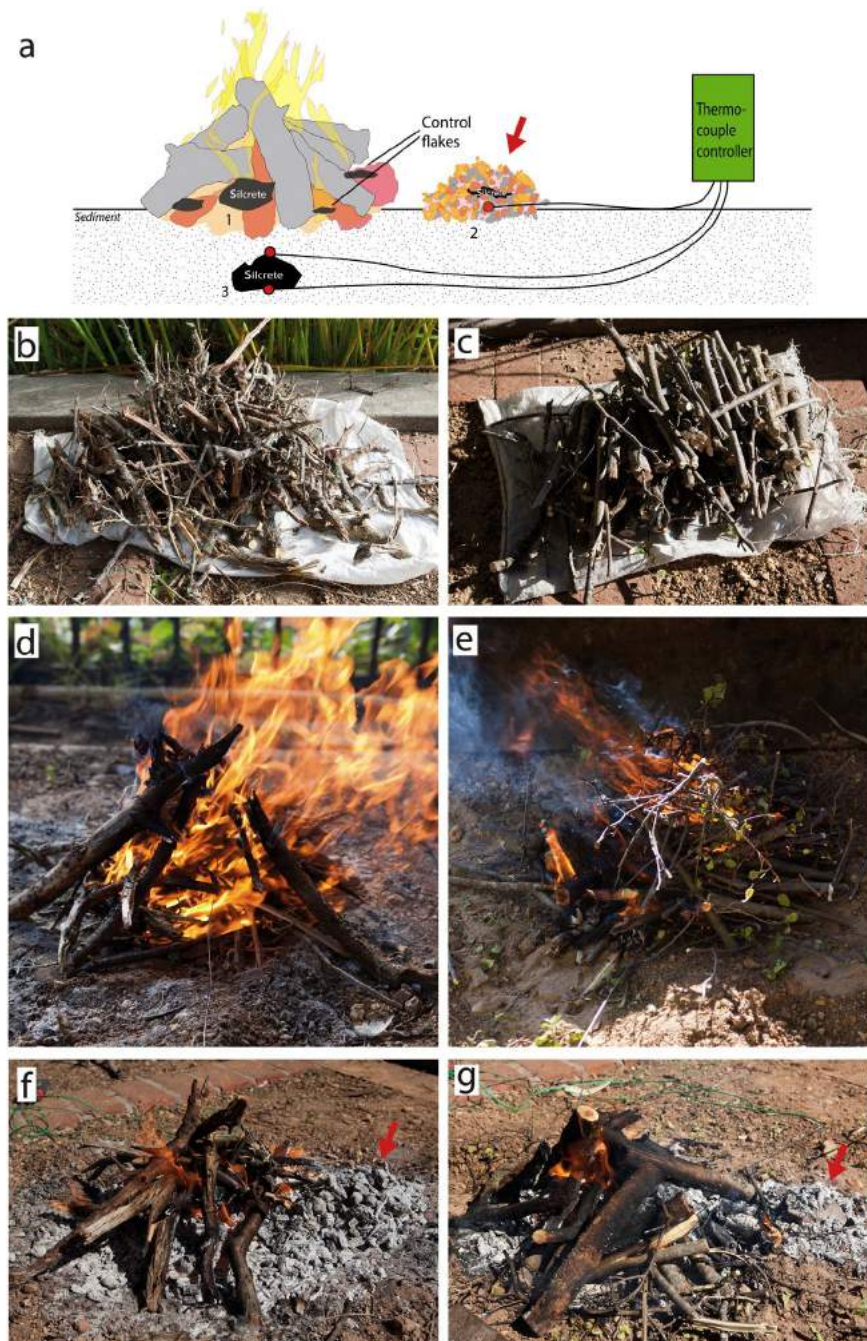


Fig. 1. Schematic experimental setup of the burning experiments (a) and photos taken during the two experiments with dry (b,d,f) and green (c,e,g) *Searsia laevigata* wood. Red arrows in a, f and g mark silcrete pieces heat-treated under the piles of embers beside the fire. Numbers in (a) indicate the three different heating conditions, 1: heat treatment directly in the ash and embers cone of an open-air fire; 2: heat treatment under embers beside the fire; 3: sand-bath heat treatment.

2.2. Non tempering-residue reference material

Because tempering-residue can be macroscopically confounded with other residue potentially found on the surface of silcrete artefacts, we analysed two different types of black residue along with the experimentally produced tempering-residue. One of these is a thin black layer of charred lamb fat that we dripped onto a piece of silcrete lying on embers after a barbecue. The silcrete was left overnight on top of the embers so that the fat had sufficient time to char. The second residue is a black mat layer, most likely a type of lichen or algae, formed on the surface of a silcrete pebble from the Swartvlei source (Schmidt and Mackay 2016), a periodically dried-out lake in South Africa's Cederberg

Mountains (henceforth referred to as 'biological crust' for simplicity). The dense black biological crust and the black charred fat both resemble tempering-residue macroscopically and could potentially be mistaken for the latter (Fig. 2).

2.3. Analysis of the tempering-residue and reference

To investigate the process of formation of tempering-residue we selected one piece of silcrete covered with experimental tempering-residue for reflection microscopy. This sample was cut with a diamond-tipped rock saw perpendicular to the surfaces containing the residue, embedded in resin and polished to obtain a plane section for reflected



Fig. 2. Non-tempering-residue reference material. Left: black fat-derived char on the surface of a piece of silcrete. Right: black biological crust (most likely an algae or lichen) on the surface of a silcrete pebble.

light microscopy. The section was analysed under white reflected light using a reflected light microscope with oil immersion lenses at magnifications from 200x to 1000x.

To propose a non-destructive analytical protocol we characterised tempering-residue and non-tempering-residue reference material macroscopically and by potentially non-destructive Raman and infrared spectroscopy. The percentage of the silcrete pieces' total surface covered by tempering-residue after the heating experiments was determined using 3D scans of a Breuckmann smartSCAN^{3D}-HE scanner. Using these 3D models, the relative size of surfaces covered by residue can be calculated as a percentage of the total surface of the silcrete pieces. The organic nature of the tempering- and reference residues was verified by infrared (IR) spectroscopy in the C-H spectral region, using powder-ATR (attenuated total reflectance) analysis on powders scraped off the residue surfaces. We used a portable Bruker ALPHA infrared spectrometer for these analyses (spectra acquired between 2600 and 3100 cm^{-1} , resolution 4 cm^{-1}). These spectra are comparable with the ones acquired non-destructively using micro-ATR-IR on the surface of artefacts as in Schmidt et al. (2015a). Additionally, we also acquired non-destructive Raman spectra between 800 and 1800 cm^{-1} from the surface of the samples with a Horiba Jobin Yvon HR800 spectrometer equipped with Notch Bragg Grate filters, an Ar⁺ laser excitation (wavelength 514 nm) and a 600 lines/mm grating. The spectrometer was calibrated using the 520.5 cm^{-1} band of a Si crystal.

3. Results

3.1. Formation of tempering-residue

Our fires of both dry and green *S. laevigata* wood burned for approximately 1h45. The fire from dry wood was burning steadily after 5 min, having formed an ash/embers cone at the base, with almost no smoke. The fire from green wood needed approximately 15 min to burn steadily and produce an ash/embers cone. The green wood fire produced a large quantity of thick smoke. Embers at the surface with free access to oxygen glowed at ~680°C in the dry wood experiment and at ~570°C in the green wood experiment. Temperatures in the inner part of the ash/embers cone where access to oxygen is restricted were ~480°C for dry wood and ~450°C for green wood. The temperature of the flames in both experiments was ~860°C.

3.1.1. The dry *S. laevigata* experiment

The heating experiment with dry wood produced no heat-induced fracturing in the 3 treat-treated silcrete pieces or any of the 10 control flakes. Maximum temperatures in the sand-bath were between 210°C

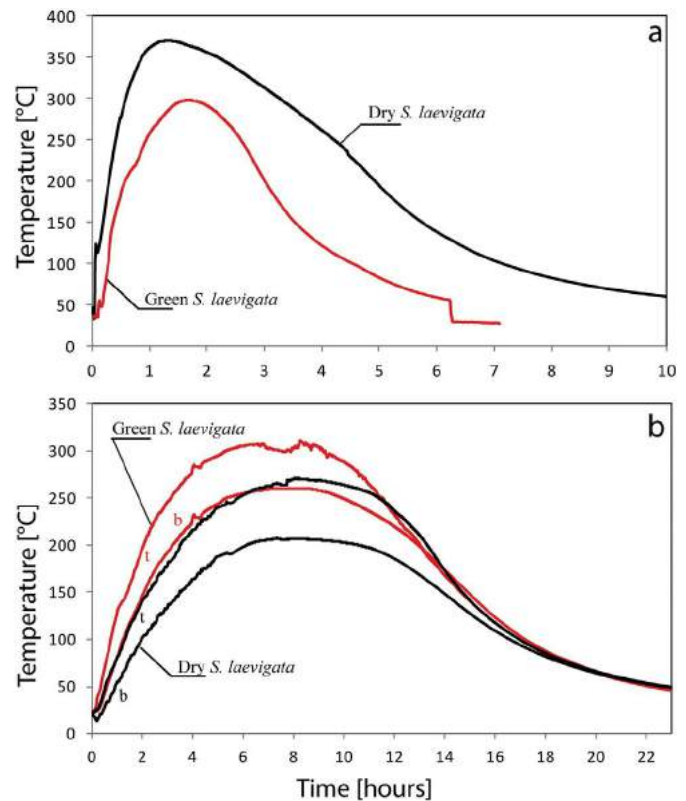


Fig. 3. Temperature curves recorded during the burning experiments. (a) Heat treatment in embers beside a fire. The K-type thermocouples were placed on the ground below the heat-treated silcrete piece and arranged for them not to measure temperatures of the embers but of the silcrete itself. (b) Heat treatment in a sand-bath beneath a fire. The curves marked *t* were recorded by the thermocouple on top of the silcrete piece, the curves marked *b* below it.

and 270°C and the effective ramp rates were 0.5–0.7 °/min (Fig. 3b), whereas the heat treatment under embers beside the fire produced a maximum temperature of 370°C under the silcrete with a ramp of 4.5°/min. Temperature curves recorded during sand-bath heating and heat treatment under embers beside the fire are compared in Fig. 3. In the cases of both these heat treatment techniques, the duration at or close to maximum temperatures was over one hour, indicating that all thermal transformations were achieved for the treatment to be a success (Schmidt et al. 2015b). Removing a flake from each of the pieces heat-treated with the three heating techniques (sand-bath, under the pile of embers and in the ash/embers cone) produced smooth post-heat treatment (post-HT) fracture surfaces that are clearly visible and contrast with the relatively rougher pre-HT surfaces. The difference between pre-heating and post-heating surfaces appears equally pronounced in all pieces regardless of the heating environment.

None of the silcrete pieces nor any of the control flakes heat-treated with dry *S. laevigata* wood showed any sign of black residue or surface deposit (Fig. 4).

3.1.2. The green *S. laevigata* experiment

The heating experiment with green *S. laevigata* wood produced heat-induced fracturing in one of the heated silcrete control flakes (lower left in Fig. 5). All other pieces (the 9 control flakes and the 3 pieces heat-treated with the three different heating techniques) remained intact. Silcrete in the sand-bath was heated to temperatures between 260°C and 310°C with a ramp of 0.6–0.8 °/min (Fig. 3b). These results show that the green wood experiment produced slightly higher temperatures in the sand-bath than the dry wood experiment. The embers heating environment beside the fire produced 300°C

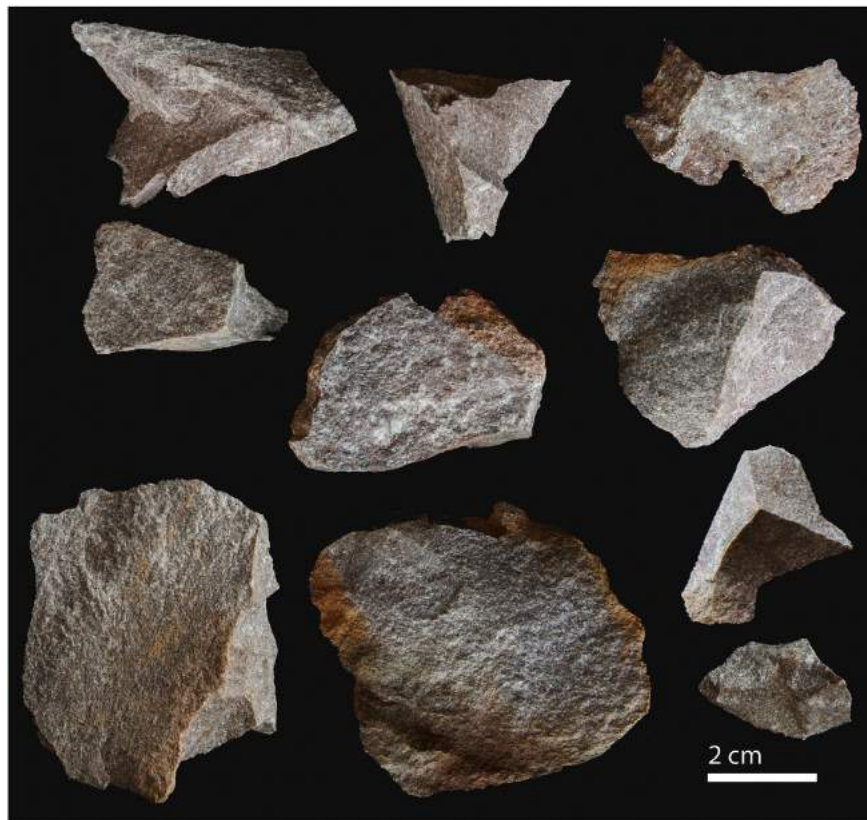


Fig. 4. Control flakes from the ash and embers cone of a fire lit from dry *Searsia laevigata* wood. Note that no tempering-residue formed on their surface.

under the silcrete with a ramp of 3°/min (Fig. 3a), thus lower temperatures than during the dry wood experiment. However, these lower temperatures may be caused by slight differences in the experimental

protocol (for example the exact quantity of embers used) and not by the moisture content of the wood. Flakes knapped from the three pieces of silcrete heat-treated with the three different techniques have smooth

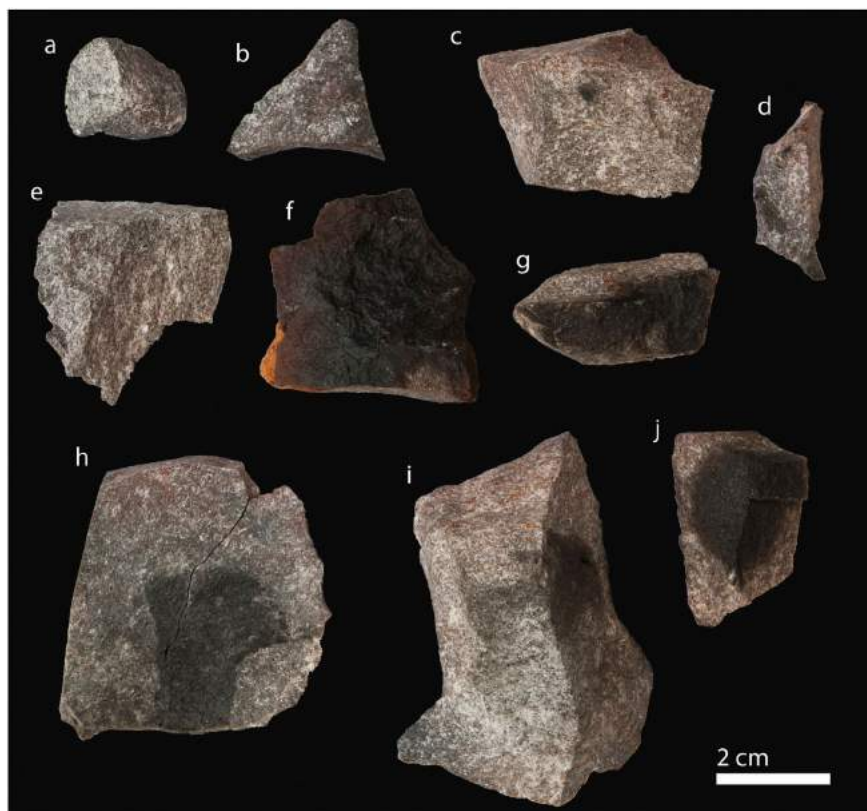


Fig. 5. Control flakes from the ash and embers cone of a fire lit from green *Searsia laevigata* wood. Note that seven of the ten pieces show traces of tempering-residue on their surface.



Fig. 6. Silcrete pieces heat-treated in the ash and embers cone of a fire lit from green *Searsia laevigata* wood. The surface covered by black tempering-residue corresponds to the bottom of the piece within the fire.

post-HT surfaces similar to the ones produced during the dry wood experiment.

The silcrete piece heated in the sand-bath (condition 1 of Section 2.1) and the pieces heated under embers beside the fire (condition 2) both showed no signs of black residue on their surface (Supplementary Fig. 3). However, seven out of the ten control flakes (Fig. 5) and the 115 cm³ piece directly heated in the ash and embers cone (condition 3, Fig. 6) show traces of tempering-residue. Percentages of the surfaces covered by residue on these pieces as determined by 3D surface scans are summarised in Table 2. In one case it was possible to record the orientation of the piece covered by residue (the piece heated in the ash and embers cone, cf. Fig. 6) to determine which side was affected by tempering-residue. Only the lower surface (bottom of the piece) was covered by a layer of residue that reached around the edge of this bottom surface, also affecting the lower part of one of the lateral surfaces (Fig. 6). 33 % of the surface of this piece was covered by residue and 1.8 – 26 % of the surfaces on six of the seven control flakes show traces of residue (Table 2). One of the control flakes (Fig. 5c) was not scanned because it only shows a very small spot of residue (<1 %) on its surface. Thus, tempering-residue, when produced, did not cover the entire surface of the heat-treated silcrete pieces but rather a limited percentage of their total surface (one third at maximum during our experiments).

3.2. Analytical characterisation of tempering-residue

3.2.1. Microscopic structure of tempering residue

The microscopic section of tempering-residue shows a 10–20 μm thick film on the silcrete surface (Fig. 7). The overall reflectance value is low as typical for organic wood tar (Crelling et al. 2006). Fusinite and μm-sized charcoal (inertodetrinite) inclusions, resulting from the residue's formation in the proximity of embers or ashes of the wood fire, can be recognised by their characteristic high reflectance values (Taylor et al. 1998). Pores formed by melt degassing indicate a formation as a hot liquid. Fusinite and inertodetrinite are the result of incomplete burning of lignin or cellulose containing tissues (Taylor et al. 1998), hence indicating anoxic conditions during the formation of the residue. These characteristics, already observed in an earlier work

(Schmidt et al. 2015a), appear to be characteristic for tempering-residue.

3.2.2. A non-destructive analytical protocol

Macroscopically all three analysed residues, tempering-residue, biological crust and fat-derived char, are similar. Although slight differences in their surface structure can be observed at magnifications between 20x and 50x, tempering-residue and biological crust are so similar that their distinction without reference material appears to be difficult. However, fat-derived char clearly has a different surface structure, showing a somewhat smoother and shinier surface. These differences are illustrated in Fig. 8.

Spectroscopic analysis of the tempering-residue along with the reference samples of burned fat and biological crust revealed some features that can be used to characterise these products. Infrared spectroscopy of all three residues produced two sharp CH bands near 2900 cm⁻¹ (Fig. 9b). The quality of our spectra is not sufficient to observe clear difference in band-shape or wavenumber although some variation in shape can be noticed. Raman spectroscopy on the other hand produced different spectra of the residues (Fig. 9a). Tempering-residue shows the two typical bands of sp² hybridised carbon near 1600 cm⁻¹ (G-band) and sp³ hybridised carbon near 1370 cm⁻¹ (D-band), indicating carbonisation of organic substances (Tomasini et al. 2012). Burned fat produced similar Raman bands, but of lower intensity and with a different D/G-band ratio. Biological crust however, has a significantly different Raman spectrum revealing a supplementary band near 1243 cm⁻¹ and a shoulder at 1655 cm⁻¹. Thus, the unburned biological crust can be confidently distinguished from carbonised products on the basis of non-destructive Raman spectroscopy.

4. Discussion

4.1. The formation of tempering residue

Our results suggest that tempering-residue forms by distillation of plant exudations and deposition of the produced gaseous phase on the silcrete surface. This is illustrated by the residue only covering the bottom and a portion of the lateral surfaces on the silcrete piece for which we recorded orientation in the fire's ash/embers cone. The presence of degassing pores in the residue indicates that the gaseous phase first condenses on the surface and the liquid then solidifies in a second step. At least partially anoxic conditions, hindering this liquid from combusting, are most likely the condition for the formation of tempering-residue. This hypothesis is further strengthened by the presence of Fusinite and inertodetrinite, both results of incomplete burning in anoxic conditions. Such a mode of deposition makes it highly unlikely that the gaseous phase could penetrate sand below a burning fire and form tempering residue on silcrete heated in a sand-bath. Our results also suggest that the formation of tempering-residue is only possible if the burned wood contains sufficient moisture that can be vaporised to trigger the distillation.

Thus, the first two research questions we asked in the introduction can be answered after our experiments. [1] Tempering-residue was only produced during heat treatment in embers heating environments. Sand-bath heating did not produce tempering-residue, although the

Table 2

Results of the surface ratios covered by tempering-residue during the green wood experiment as determined on the base of 3D surface scans.

Piece ID	Photo	Total surface area [mm ²]	Area covered by tempering-residue [mm ²]	% of surface covered by tempering-residue
Control flakes	Fig. 5i	7241.17	307.94	4.3 %
	Fig. 5d	2929.16	51.36	1.8 %
	Fig. 5j	2021.15	522.08	26 %
	Fig. 5g	2992.42	308.99	10 %
	Fig. 5f	3956.81	675.63	17 %
	Fig. 5h	5579.75	703.97	13 %
Heated in the fire (condition 3)	Fig. 6	17324.08	5677.96	33 %

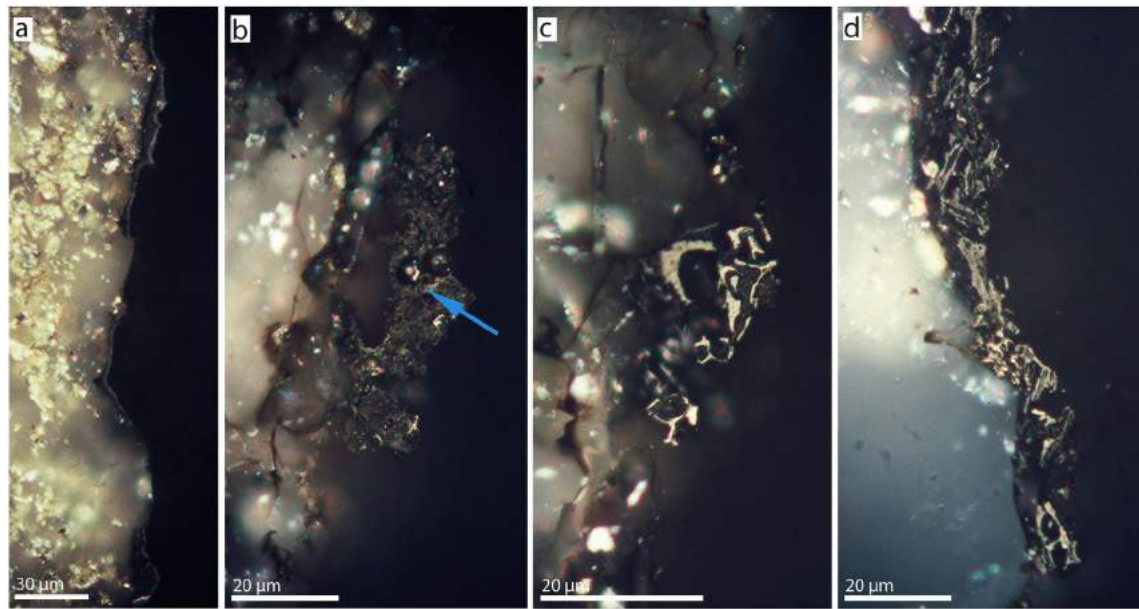


Fig. 7. Micrographs of a cross-section through *S. laevigata* tempering-residue. (a) Overview showing a thin continuous film of tar on the surface of the silcrete. (b) Detail of the residue showing the low reflectance of wood tar and pores formed by melt degassing (one pore is marked by the blue arrow). (c) Detail of the residue showing inertodetrinite inclusions with higher reflectance in a cement of tar with lower reflectance values. (d) Fusinite on the surface of the silcrete with higher reflectance showing the characteristic features of the plant structure. Reflected white light.

sediment used as a heating environment did contain organic material such as pieces of dead wood, leaves and grass. For research question [2], our data indicate that only green wood leads to the formation of tempering-residue, implying that the presence of the latter on heat-treated artefacts can be used as a proxy for the use of freshly cut wood

to heat-treat silcrete. Whether the mixture of green and dry wood also produces tempering-residue remains to be determined, though it appears likely. Regardless, dead wood lying around on the ground and accidentally or intentionally buried along with silcrete during sand-bath heating does not produce tempering-residue because dead wood can

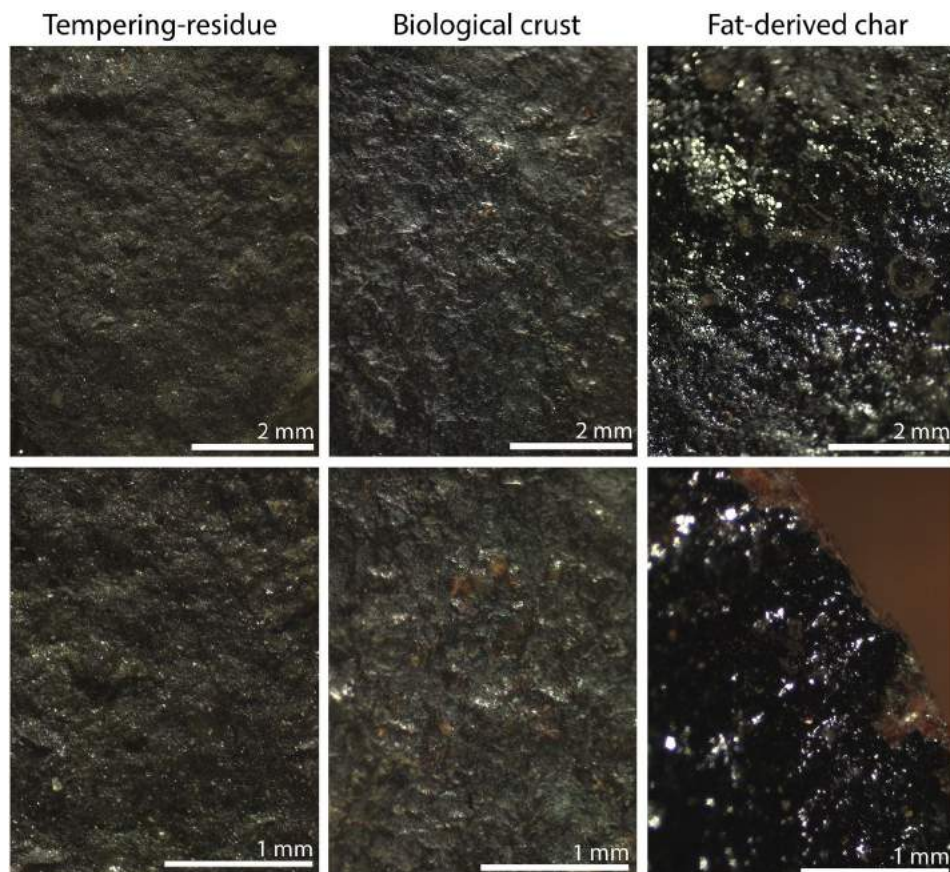


Fig. 8. Surface micrographs of tempering residue (left), biological crust (middle) and fat-derived char (right) at two different magnifications.

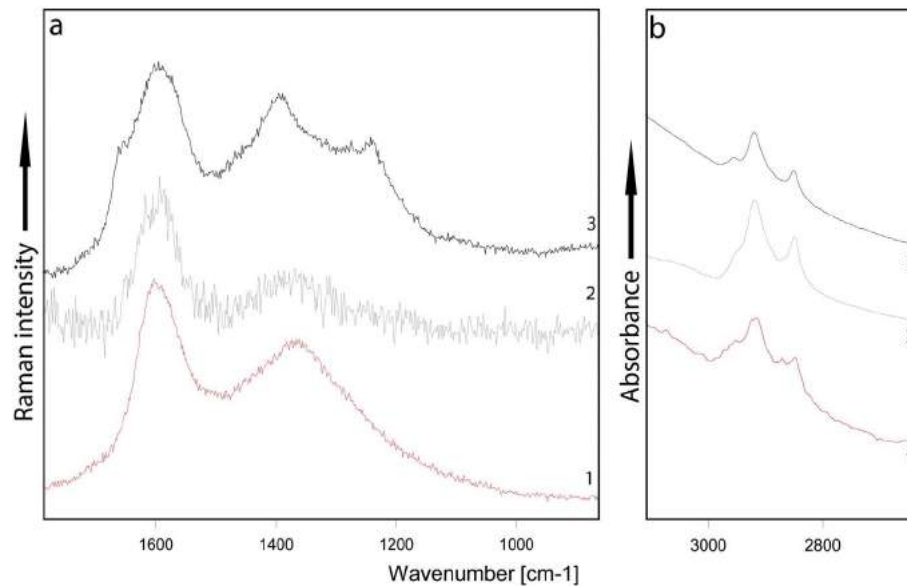


Fig. 9. Spectroscopic analysis of tempering-residue (1), fat-derived char (2) and biological crust (3). (a) Raman spectra, (b) infrared ATR spectra. Spectra vertically offset for readability.

be expected not to contain sufficient moisture to trigger the dry distillation. Tempering-residue on artefacts can therefore be considered a proxy for heat treatment in the embers of open-air fires.

Research question [3] can only be partially answered. Our experimental setup did not take into account that under real-life conditions different wood types may have been used in a single fire or that real-life fires may have been lit from dry and green wood together. However, it appears clearly that only a small portion of the affected silcrete pieces' total surface actually showed traces of residue in our experiment. The residue containing portion of the pieces' surface was between 1 and 33 % of their total outer surface. If we had knapped flakes from one such piece with tempering-residue, only a small number of the resulting flakes would actually show traces of the residue. Thus, already a small number of silcrete artefacts with traces of tempering-residue may indicate that a rather large number of all heat-treated silcrete blocks were in contact with embers of a fire.

4.2. A non-destructive analytical protocol

Research question [4], relating to whether it is possible to distinguish tempering-residue from other residues non-destructively cannot be answered unambiguously, although a few observed criteria allow for some basic distinctions. Macroscopically, tempering-residue cannot be distinguished from biological crust and fat-derived char. The observation with a stereo-microscope at low magnifications identifies burned fat because its surface is smoother and shinier than the surface of tempering residue. However, after our experimental study it remains completely unclear how taphonomic processes affect the surface aspect of such residues so that stereo-microscopic observations cannot be proposed as a potential analytical tool for identifying archaeological tempering residue.

Infrared spectroscopy on the other hand allows a good distinction between organic residues (tempering residue, fat-derived chars, biological crust) and inorganic mineral deposits (manganese oxide/hydroxides) due to the presence of CH-bands in the former. Previous studies on tempering residue have shown that such CH-bands can be preserved over at least the last part of the MSA (Schmidt et al. 2015a), so that taphonomy can be expected to have little influence on such infrared spectroscopic analyses. Raman spectroscopy allows the differentiation of residues formed by biological agents, like algae/lichen, because their CC-band region shows more than only D- and G-bands of amorphous carbon. Substances formed by charring of organic matter show a clear D/G-band massive with these two bands only (Tomasini et al. 2012).

The Raman signal caused by amorphous and graphitic carbon has been reported to be stable over geological time periods (Muirhead et al. 2012) so that taphonomy appears highly unlikely to be a factor for such Raman spectroscopic analyses. Whether burned biological crust produces a surface deposit resulting in a similar Raman D/G-band spectrum remains to be investigated in the future. As it stands, the combined use of infrared and Raman spectroscopy, if infrared-CH-bands and Raman-D/G-bands are recognised, positively identifies the analysed residue as an organic solid transformed by heat. If the analysed residue is strictly associated with pre-heating fracture scars (i.e. with the initial outer surface of the silcrete pieces during its heat treatment that formed during a first stage of knapping or preforming), it can confidently be concluded that the residue formed during heat treatment.

After these non-destructive analyses, further destructive analyses may be necessary to clearly identify the residue as resulting from the dry distillation of plant exudation. Only then does the residue unambiguously demonstrate the contact of the heat-treated silcrete with the embers of an open-air fire. Such destructive analyses potentially are reflection microscopy aiming to detect structural features that are specific of the mode of formation (degassing pores, fusinite and inertodetrinite inclusions) or the reflectance value of wood tar (Crelling et al. 2006). The use of separation techniques (such as Gas-Chromatography coupled to Mass Spectrometry, GC-MS), aiming to detect specific bio-markers that document a plant origin of the residue, might be another promising venue, although future systematic studies are necessary to evaluate their potential in this context. The analytical criteria we found most helpful for detecting tempering-residue are graphically summarised in Fig. 10.

5. Conclusion

Our findings have implications for interpreting archaeological tempering-residue on heat-treated silcrete artefacts from the South African Middle Stone Age. Its presence, when associated with surfaces that correspond to the initial outer surface of the silcrete piece during its heat treatment (created by pre-heat treatment knapping, i.e. pre-heating surfaces), and even more so when also cross-cut by clean post-heating fracture scars, clearly indicates two important parameters of the heating procedure: (1) the silcrete was heat-treated in the embers of an open-air fire, possibly a regular domestic fire, and (2) at least part of the wood used for this fire was green, freshly cut, wood. Thus, tempering-residue together with heat-induced non-conchoidal (HINC) fracturing in a fire after which knapping continued (Schmidt et al. 2015a), are

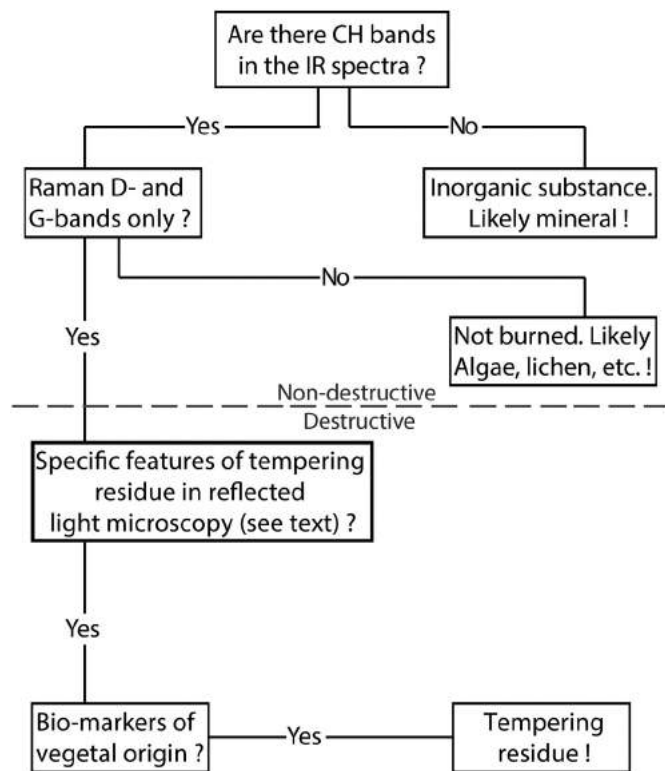


Fig. 10. Schematic pathway for detecting tempering-residue on heat-treated silcrete artefacts.

the two most promising proxies for a heating technique involving fast heating in open-air fires. Whether their absence on heat-treated silcrete artefacts may be interpreted as indicating heat treatment in open fires made from dry wood or with an alternative technique like heating in a sand bath must be decided for each archaeological case individually. It can be expected that varying preservation conditions in different sites affect the likelihood that tempering-residue is preserved. In a similar fashion, the resistance of different silcrete types to thermally-induced fracturing can also be expected to influence the frequency of HINC fractures on different assemblages of heat-treated silcrete. In either case, our results highlight that if tempering-residue is found, it can be used as a proxy for heat treatment in embers using green wood.

We also propose a non-destructive analytical protocol that distinguishes tempering-residue and other charred black residue from similarly looking residues produced by living organisms or black mineral deposits. These analyses rely on the combined use of infrared and Raman spectroscopy. Tempering-residue and fat-derived char have a similar origin, both being caused by the action of fire, and their presence on artefacts most likely has similar implications: the artefact was in contact with a fire. The association of one of these residues with pre-heating surfaces would in both cases indicate a formation during heat treatment. The differentiation between fat-derived char and wood-tar (i.e. tempering-residue), provided that the residue is found on a pre-heating surface, may therefore not be of major importance for interpreting the history of the artefact. However, in order to unambiguously use residue on heat-treated artefacts as a proxy for the direct contact between silcrete and embers, destructive analyses may be necessary. Reflection microscopy can be used to detect the characteristic features observed in tempering-residue (as highlighted in our study). The potential of separation techniques (such as GC-MS) for detecting specific bio-markers that would identify the predecessor phase (the burned wood species for example) remains to be investigated. This research should first concentrate on evaluating the possibility to sample sufficient residues from a single artefact for the analyses and on finding pertinent bio-markers in tempering residue.

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Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jasrep.2016.08.014>.

References

- Bettinger, R.L., Eerkens, J., 1997. Evolutionary implications of metrical variation in Great Basin projectile points. In: Barton, C.M., Clark, G.A. (Eds.), *Rediscovering Darwin: Evolutionary Theory and Archaeological Explanation*, Archaeological Papers No. 7, American Anthropological Association, Arlington, pp. 177–191.
- Brown, K., Marean, C., 2010. Wood Fuel Availability for Heat Treatment Drives the Rise and Fall of Silcrete as a Raw Material in the Middle Stone Age of South Africa, "Abstracts of the PaleoAnthropology Society 2010 Meetings." *PaleoAnthropology 2010*, A0001–A0040.
- Brown, K.S., Marean, C.W., Herries, A.I.R., Jacobs, Z., Tribolo, C., Braun, D., Roberts, D.L., Meyer, M.C., Bernatchez, J., 2009. Fire as an Engineering Tool of Early Modern Humans. *Science* 325, 859–862.
- Crelling, J., Glikson, M., Huggett, W., Borrego, A.G., Hower, J., Ligouis, B., Mastalerz, M., Misz, M., Suárez-Ruiz, I., Valentim, B., 2006. International Committee for Coal and Organic Petrology (ICCP), Atlas of anthropogenic particles, Geological Survey Open-File Study 06-01 Indiana.
- Mourre, V., Villa, P., Henshilwood, C.S., 2010. Early Use of Pressure Flaking on Lithic Artefacts at Blombos Cave, South Africa. *Science* 330, 659–662.
- Mucina, L., Rutherford, M.C., 2006. The vegetation of South Africa, Lesotho and Swaziland, *Strelitzia 19*. South African National Biodiversity Institute, Pretoria.
- Muirhead, D.K., Parnell, J., Taylor, C., Bowden, S.A., 2012. A kinetic model for the thermal evolution of sedimentary and meteoritic organic carbon using Raman spectroscopy. *J. Anal. Appl. Pyrolysis* 96, 153–161.
- Poorter, L., Bongers, L., Bongers, F., 2006. Architecture of 54 Moist-Forest Tree Species: Traits, Trade-Offs, and Functional Groups. *Ecology* 87, 1289–1301.
- Porraz, G., Texier, P.-J., Archer, W., Piboule, M., Rigaud, J.-P., Tribolo, C., 2013. Technological successions in the Middle Stone Age sequence of Diepkloof Rock Shelter, Western Cape, South Africa. *J. Archaeol. Sci.* 40, 3376–3400.
- Schmidt, P., 2016. The 'Sand-Bath' and Lithic Heat Treatment in the South African Middle Stone Age: Myth or Reality? *Afr. Archaeol. Rev.* <http://dx.doi.org/10.1007/s10437-016-9217-z> (published online since 23/04/2016).
- Schmidt, P., Mackay, A., 2016. Why Was Silcrete Heat-Treated in the Middle Stone Age? An Early Transformative Technology in the Context of Raw Material Use at Mertenhof Rock Shelter, South Africa. *PLoS One* 11, e0149243.
- Schmidt, P., Porraz, G., Słodczyk, A., Bellot-gurlet, L., Archer, W., Miller, C.E., 2013. Heat treatment in the South African Middle Stone Age: temperature induced transformations of silcrete and their technological implications. *J. Archaeol. Sci.* <http://dx.doi.org/10.1016/j.jas.2012.10.016> 40, 3519–3531.
- Schmidt, P., Porraz, G., Bellot-Gurlet, L., February, E., Ligouis, B., Paris, C., Texier, J.P., Parkington, J.E., Miller, C.E., Nickel, K.G., Conard, N.J., 2015a. A previously undescribed organic residue sheds light on heat treatment in the Middle Stone Age. *J. Hum. Evol.* 85, 22–34.
- Schmidt, P., Paris, C., Bellot-Gurlet, L., 2015b. The investment in time needed for heat treatment of flint and chert, *Archaeol Anthropol Sci* published online since 03/07/2015 (DOI: 10.1007/s12520-015-0259-y, 1–10).
- Summerfield, M.A., 1983. Petrography and diagenesis of silcrete from the Kalahari Basin and Cape coastal zone, Southern Africa. *J. Sediment. Res.* 53, 895–909.
- Taylor, G.H., Teichmüller, D.A., Diessel, C.F.K., Littke, R., Robert, P., 1998. *Organic Petrology*. Gerbrüder Borntraeger, Berlin.
- Tomasini, E.P., Halac, E.B., Reinoso, M., Di Liscia, E.J., Maier, M.S., 2012. Micro-Raman spectroscopy of carbon-based black pigments. *J. Raman Spectrosc.* 43, 1671–1675.
- Tribolo, C., Mercier, N., Douville, E., Joron, J.L., Reyss, J.L., Rufer, D., Cantin, N., Lefrais, Y., Miller, C.E., Porraz, G., Parkington, J., Rigaud, J.P., Texier, P.J., 2013. OSL and TL dating of the Middle Stone Age sequence at Diepkloof Rock Shelter (South Africa): a clarification. *J. Archaeol. Sci.* 40, 3401–3411.
- Wadley, L., 2013. Recognizing Complex Cognition through Innovative Technology in Stone Age and Palaeolithic Sites. *Camb. Archaeol. J.* 23, 163–183.
- Wadley, L., Prinsloo, L.C., 2014. Experimental heat treatment of silcrete implies analogical reasoning in the Middle Stone Age. *J. Hum. Evol.* 70, 49–60.