Journal of Archaeological Science xxx (2017) 1–20

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Heat-induced alteration of glauconitic minerals in the Middle Stone Age levels of Blombos Cave, South Africa: Implications for evaluating site structure and burning events

Magnus M. Haaland [a, *], David E. Friesem [b], Christopher E. Miller [c, d], Christopher S. Henshilwood [a, e]

[a] Department of Archaeology, History, Cultural Studies and Religion, University of Bergen, Øysteinsgate 1, PO Box 7805, N-5020 Bergen, Norway
[b] McDonald Institute for Archaeological Research, University of Cambridge, Downing Street, Cambridge CB2 3ER, UK
[c] Institute for Archaeological Sciences, University of Tübingen, Rümelinstr. 23, 72070 Tübingen, Germany
[d] Senckenberg Center for Human Evolution and Paleoenvironment, University of Tübingen, Rümelinstr. 23, 72070 Tübingen, Germany
[e] Evolutionary Studies Institute, University of the Witwatersrand, P.O. WITS, 2050 Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form
5 June 2017
Accepted 11 June 2017
Available online xxx

Keywords:
Middle Stone Age
Site structure
Hearth
Combustion feature
Fire proxy
Fire experiment
FTIR
Micro-FTIR
Spatial analysis
GIS
Colourimetry
Micromorphology

ABSTRACT

In this paper we conduct geochemical and colourimetric measurements of glauconite grains in micromorphological thin sections from the Middle Stone Age site of Blombos Cave, South Africa, to investigate the formation, internal structure and reworking of heat-exposed cave deposits that are related to prehistoric burning events. Controlled heating experiments were first carried out on glauconite-rich loose sediments and block samples, both of which were collected from the Blombos Cave bedrock. The control samples were then subjected to Fourier transform infrared spectrometry (FTIR), microscopic Fourier transform infrared spectrometry (micro-FTIR) and petrographic-colourimetric analyses. The control experiment shows that glauconitic minerals undergo a gradual and systematic colour change when temperatures reach higher than c. 300–400 °C, primarily due to dehydration and iron oxidation. They also undergo clear structural changes when temperatures reach higher than c. 550 °C due to dehydroxylation and mineral transformation. By assessing the nature and degree of heat-induced optical and molecular alteration in glauconitic minerals, we demonstrate how glauconite grains in thin sections can be classified by the temperature to which they were exposed (20–400 °C, >400 °C, >600 °C and >800 °C). To assess the archaeological relevance of our controlled heating experiment, we applied this glauconite classification scheme to >200 grains found in three micromorphological thin sections of a Middle Stone Age (MSA) combustion feature. These grains were individually geo-referenced within the local coordinate system of Blombos Cave, through a thin-section-based GIS mapping procedure. With improved spatial control, we were able to study both the general distribution of non-altered and heat-altered glauconite grains in their original sedimentary context, as well as to calculate heat distribution models that cover the entire sampled section. This combined geo-chemical, optical and spatio-contextual approach provides insights into more elusive aspects of MSA site structure and burning events, such as heat intensity, burning frequency, temperature distribution, internal hearth structure and post-depositional reworking. The workflow we propose may easily be implemented and adapted to other archaeological contexts and to analogous sedimentary materials that show comparable heat-induced alteration patterns.

1. Introduction

Archaeologists routinely use the presence or absence of evidence for fire, as well as the size, placement and frequency of hearths, to infer prehistoric site structure and fire-related human activities (e.g. Henry et al., 1996; Wadley, 2006; Vallverdú et al.,

* Corresponding author.
E-mail address: magnus.haaland@uib.no (M.M. Haaland).

http://dx.doi.org/10.1016/j.jas.2017.06.008

2012; Shahack-Gross et al., 2014). However, several studies demonstrate that our ability to properly recognise and evaluate burnt contexts, macroscopically in the field, can be limited (Mentzer, 2012; Mallol et al., 2013). At some sites an intact, unlined open hearth can only be recognised by the presence of a reddened substrate, overlain by thin layers of charcoal and ash constituting a predictable trifold structure (Canti and Linford, 2000; Mentzer, 2012; Friesem et al., 2014b). Yet at many sites, as in the case of the Middle Stone Age (MSA) and Later Stone Age (LSA) layers at Blombos Cave, South Africa (Fig. 1), the identification of a structurally intact hearth versus a post-depositionally disturbed, redeposited or mixed burnt deposit can be more difficult, since the physical preservation of burnt deposits is variable and the quartz-rich substrate does not easily rubify.

Blombos Cave is located in Blombosfontein Nature Reserve (3.5 km2), c. 300 km east of Cape Town on the southern coast of South Africa (Fig. 1a). The lower part of the 3 m deep cave sequence is comprised of laminated deposits that contain MSA artefacts and features dated to ca. 101–70 ka (Fig. 1b and c) (Henshilwood et al., 2011; Jacobs et al., 2013). Several unlined, discrete hearths, combustion features and other fire-related deposits containing ash, charcoal and burnt sediments have been documented within the MSA deposits (Henshilwood et al., 2001; Henshilwood, 2005). While the charcoal shows variable preservation, much of the original ash has recrystallized and mixed with the calcareous-rich matrix. In addition, numerous millimetre thick lenses of black, humified and non-burnt material are frequently encountered within the cave deposits. In the field, the appearance of these black lenses is similar to that of burnt or charred material. Consequently, it is hard to tell from the location and nature of macroscopic observations whether specific deposits inside the cave truly were burnt, whether they were burnt *in-situ* or whether they could have been reworked or redeposited.

Many studies have, however, demonstrated that heat exposed sediments, e.g. sediments directly below an open fire, show indications of having been altered when examined microscopically (Canti and Linford, 2000; Berna et al., 2007; Karkanas et al., 2007; Mallol et al., 2007; Berna et al., 2012; March et al., 2014; Shahack-Gross et al., 2014; Aldeias et al., 2016). In a number of archaeological contexts, the effects of high temperatures on the molecular structure of sedimentary components has been successfully examined using both bench Fourier transform infrared spectrometry (FTIR) on bulk samples (Weiner, 2010) and microscopic FTIR (micro-FTIR) on thin sections (e.g. Berna et al., 2012; Goldberg et al., 2012; Shahack-Gross et al., 2014; Villagran et al., 2017).

The sedimentary infilling of Blombos Cave is driven partly by the granular disaggregation of the cave wall and ceiling, and partly by input from exterior aeolian processes. The cave is formed in the Mio-Pliocene shallow marine and aeolian deposits of the De Hoopvlei and the Wankoe formations (Malan, 1990; Malan et al., 1994) and the interior sediments thus consist primarily of unconsolidated, calcareous quartz-rich silt and sand. We also find a high abundance (>100 per 1 cm^2) of green, sand-sized and pellet-shaped minerals that derive from the bedrock and that are randomly distributed within the excavated deposits (Fig. 2). Based on their optical characteristics and a comparison of their FTIR spectra with published spectra, we confirmed that they are glauconitic minerals (see Fig. 3 and Table 1; Odin et al., 1988; Chukanov 2014).

Similar to many sheet silicate minerals, glauconite grains can alter their colour and chemical composition due both to weathering processes (McRae, 1972; Pestitschek et al., 2012) and exposure to heat (Ramaswamy and Kamalakkannan, 1995; Hajpál and Török, 2004; Pavlyukevich et al., 2005; Basso et al., 2008). Encouraged by the abundance of glauconitic grains within the Blombos Cave deposits and confronted with the preservation state and complexity of the combustion features at this site, the aim of this study is to investigate a new proxy (glauconite) to examine site formation processes associated with prehistoric burning events, and to develop a spatio-contextual framework in which this proxy can be practically applied to oriented archaeological sediment samples. Our specific objectives are threefold:

(1) Identifying and characterizing burnt glauconite grains, using geological control samples heated to known temperatures as a reference;
(2) Reconstructing the temperatures to which grains in archaeological thin sections were exposed, using FTIR, micro-FTIR and petrographic colourimetry;
(3) Mapping the spatial distribution of burnt and unburnt glauconitic grains in the archaeological samples, by importing geo-referenced, high-resolution thin section scans and orthophographic sections photos into a GIS application.

To demonstrate this framework's potential in identifying and evaluating prehistoric fire and burning events, we include a case study on a micromorphological block sample collected from a combustion feature in the lower part of the MSA sequence in Blombos Cave (BBC-13-14).

2. Properties of glauconitic minerals

2.1. Mineralogy and chemical properties

Glauconite belongs to a group of compositionally heterogeneous, dioctahedral, potassium and iron-rich phyllosilicates, with the general chemical formula: (K,Na) (Mg,Fe^{2+},Fe^{3+}) (Fe^{3+},Al) $(Si,Al)_4O_{10}(OH)_2$. In the structure of glauconitic mica, each layer consists of two silica tetrahedral sheets facing one central octahedral sheet (similar to 2:1 type clay minerals) (Grim, 1968; Odin et al., 1988; Dooley, 2006). In a fresh state, glauconitic grains show an ovoidal or spheroidal morphology and range in size from 1 mm (coarse sand) to clay size. The colour of glauconitic minerals range from dark olive or pale green (fresh) to yellowish or brownish green (weathered) in plane polarized light (Dooley, 2006; Basso et al., 2008; Pestitschek et al., 2012). The nuances in the green colour are related to the relative amounts of iron and aluminium present in the mineral, as well as the ratio between the divalent and trivalent iron ions (McRae, 1972). McRae (1972) reports that oxidation of structural iron due to natural weathering, especially in soils, can cause the glauconite grains to produce a heterogeneous, rusty-brown colour. The rusty parts are primarily distributed around the rim of the grain, or along weathering-induced cracks that often disrupt the grain's pellet-shaped morphology (cf. supplementary fig. A.1 for weathered grains from Blombos Cave). In South African contexts, the occurrence of “black glauconite” pellets have previously been reported by Wigley and Compton (2007), yet these grains also show a distinct green colour in thin section (Compton, John, Personal Communication, E-mail, April 21, 2017).

2.2. Infra-red spectra (transmission) of glauconite

Many researchers have studied the IR spectra of Fe–Mg dioctahedral micas (e.g. Farmer, 1974; Marel et al., 1976; Slonimskaya et al., 1986; Odin, 1988; Chukanov 2014), including archaeologists (Affonso and Pernicka, 2001), and they have reported that in glauconite, high-frequency absorption bands are observed around 3600 cm^{-1} (υ $Al^{3+}.Mg^{3+}$ –OH), 3560 cm^{-1} (υ $Fe^{3}+.Fe^{3+}/Fe^{3+}.Mg^{2+}$ –OH) and 3535 cm^{-1} (υ $Fe^{3+}.Fe^{2+}$ –OH); all of which have been associated with the stretching vibrations of hydroxyl groups (cf. Fig. 1 and Table 1). A broad and variable band near 3400 cm^{-1} has

Please cite this article in press as: Haaland, M.M., et al., Heat-induced alteration of glauconitic minerals in the Middle Stone Age levels of Blombos Cave, South Africa: Implications for evaluating site structure and burning events, Journal of Archaeological Science (2017), http://dx.doi.org/10.1016/j.jas.2017.06.008