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# Microscale distribution and concentration of preserved organic molecules with carbon–carbon double bonds in archaeological ceramics: relevance to the field of residue analysis

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## ABSTRACT

Biologically produced compounds preserved in ancient ceramics can provide invaluable information on the vessel contents. Analysis and interpretation of these so-called archaeological "residues" is therefore important for understanding and reconstructing aspects of social and cultural behaviors of ancient societies. Based on the reaction of unsaturated compounds with iodine, we developed and apply two new methods. The first is a simple and relatively rapid method for assessing the amounts of unsaturated compounds in archaeological ceramics using X-ray fluorescence (XRF). We show that this method is a reliable indicator for assessing the general preservation state of the organic material and therefore a potential pre-screening method for identifying ceramic samples suitable for organic residue analysis. The second complementary approach, based on the same iodine reaction, makes it possible to map the unsaturated molecules on ceramic surfaces at a scale that enables to correlate organic matter distribution and the underlying mineral grains using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) detector. With this method we show that the extent of adsorption of lipids onto ceramic surfaces varies with the surface properties of the different minerals in the ancient ceramic, with calcium containing minerals showing the highest affinity for compounds with unsaturated bonds. The ceramic substrate therefore influences the types of organic compounds bound and hence preserved in the ceramic. Fundamental information obtained using this method is essential for better interpreting molecular assemblages extracted from archaeological ceramics.

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## 1. Introduction

Organic compounds preserved within ceramics from archaeological sites often provide invaluable information on the contents of the vessel, and this in turn may provide information on, for example, agricultural practices, diet and trade (Heron and Evershed, 1993). Identifying vessels with preserved compounds, extracting the compounds from the ceramic and interpreting the significance of the extracted assemblage is challenging. Lipids are among the more commonly preserved molecules in ceramics (Eglinton and Logan, 1991; Evershed, 1993; Evershed et al., 2001). Other organic molecules such as proteins (Craig et al., 2000; Craig and Collins, 2002; Barker et al., 2012) and polysaccharides (Oudemans and Boon, 1991; Garnier et al., 2003; Oudemans et al., 2007) may also be preserved.

Many vessels preserved in archaeological sites do not have visible charred remains, nor any indicative extractable organic molecules from within the ceramic material (commonly referred to as "residues"). One reason could be that they are not preserved at all. Relatively warm and humid environmental conditions are assumed to be less conducive to preservation (Evershed, 2008). Another reason for the absence of any preserved molecules is that the ceramic was at some time during its history exposed to temperatures above 100–150 °C, which degrades the compounds (Namdar et al., 2011). This can occur rather frequently in archaeological sites. Alternatively, the vessels do have preserved organic compounds, but the procedure used to extract the compounds is not effective.

The majority of residue analysis studies are based on organic solvent extractable lipids. The most commonly used extraction method involves organic solvents based to some extent on the classical Bligh and Dyer method of extraction and total lipid

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determination using a polar mixture of chloroform (or dichloromethane) and methanol (Bligh and Dyer, 1959). This method however may not extract all compounds and the existence of a "bound insoluble" phase that is not extractable with organic solvents is well recognized (Regert et al., 1998, Evershed et al., 2002, Craig et al., 2004, Hansel et al., 2011). It has been shown that an acid extraction, for example, may remove additional molecules not extracted by the standard solvent extraction procedure (Stern et al., 2000). Such differential extraction may depend not only on the chemical properties of the compounds themselves, but also on the manner in which they bind to the different mineral substrates present within the ceramic. In such a case the assemblage of molecules that is extracted is also influenced by the composition of the ceramic itself; one focus of this study.

Here we exploit a well-known chemical reaction that involves iodine vapor reacting with carbon–carbon double bonds in so-called unsaturated compounds to address some of the above problems. Iodine vapor is one of the oldest methods used for staining lipids and proteins for histological purposes (Lewis and Lewis, 1915; Lewis, 1921, 1922; Cunningham Rs and S., 1926) The reaction is based on the iodination reaction with unsaturated and aromatic compounds (Rapport and Norton, 1962; Carey and Sundberg, 2007). The iodination reaction is also used for the determination of the degree of unsaturation, given as the iodine number, for the characterization of lipids (Milliau, 1893; Gill and Adams, 1900) and to monitor chemical reactions by developing thin layer chromatography (TLC) plates with iodine vapor (Mangold, 1961; Sims and Larose, 1962). We have developed two different, but complimentary methodological approaches to better understand residues preserved in ceramics using iodine vapor. One approach involves exposing an aliquot of powdered archaeological ceramic to iodine vapor, and then using X-ray fluorescence (XRF) to determine the quantity of iodine that reacted with the unsaturated bonds of the preserved molecules. In this way we gain an estimate of the amount of unsaturated compounds preserved in the ceramic. The second approach involves exposing fractured or polished surfaces of the ceramic to iodine vapor and then mapping the distribution of the iodine using an energy dispersive spectrometer (EDS) in a scanning electron microscope (SEM). This method provides information on the manner in which unsaturated compounds bind to different mineral substrates.

Previous studies analyzing the distribution of biomolecules in ancient ceramics were limited to the macroscopic locations of the compounds within the vessel (e.g. rim, body, base). They involved physical removal of part of the vessel, solvent extraction and chemical identification (Charters et al., 1993, Charters et al., 1995, Stern et al., 2000). Although the results led to important conclusions regarding lipid differential accumulation and preservation in different parts of the same vessel, the spatial distribution of the compounds in relation to the different mineral constituents of the ceramic was not addressed.

The fact that iodine binds only to unsaturated carbon–carbon bonds and not to all carbon–carbon bonds, is both an advantage and a disadvantage. Unsaturated bonds are widespread but relatively unstable (Regert et al., 1998). Thus the iodine vapor will preferentially detect relatively well preserved assemblages of molecules that in turn can be more reliably understood in terms of their archaeological significance. Furthermore, it is well known that unsaturated organic compounds are frequently preserved in archaeological ceramics (Regert et al., 2003; Malainey, 2007). Iodine vapor will not however detect compounds that do not have carbon–carbon double bonds.

## 2. Materials and methods

### 2.1. Ceramic samples

#### 2.1.1. Standard ceramic

Standard ceramic bowls were produced using a mixture of local clay from the Moza formation (Israel) and purchased from Yehu Clays Ltd, Israel, chalk (calcite) and sand in proportions of 60:25:15 weight %. The standard samples were fired in a kiln that was heated to 777 °C for 4 h in air. The ceramic was characterized using infrared spectroscopy (see Inline Supplementary Fig. 1).

Inline Supplementary Fig. S1 can be found online at http://dx.doi.org/10.1016/j.jas.2013.11.025.

#### 2.1.2. Archaeological samples

Archaeological samples used in this paper were collected during excavations in two different archaeological sites in Israel (Fig. 1). The first one is Tel es-Safi/Gath, located on the border between the central Shephelah (Judean foothills) and the southern Coastal Plain. The site is identified as the Canaanite and Philistine city of Gath (Rainey, 1975; Maeir, 2008, 2012) .The vessels analyzed are from Iron Age strata dated to the ninth century BCE. The second site is Ramat Rahel located on the south-eastern outskirts of modern Jerusalem. The vessels analyzed are from a pit in which vessels dating

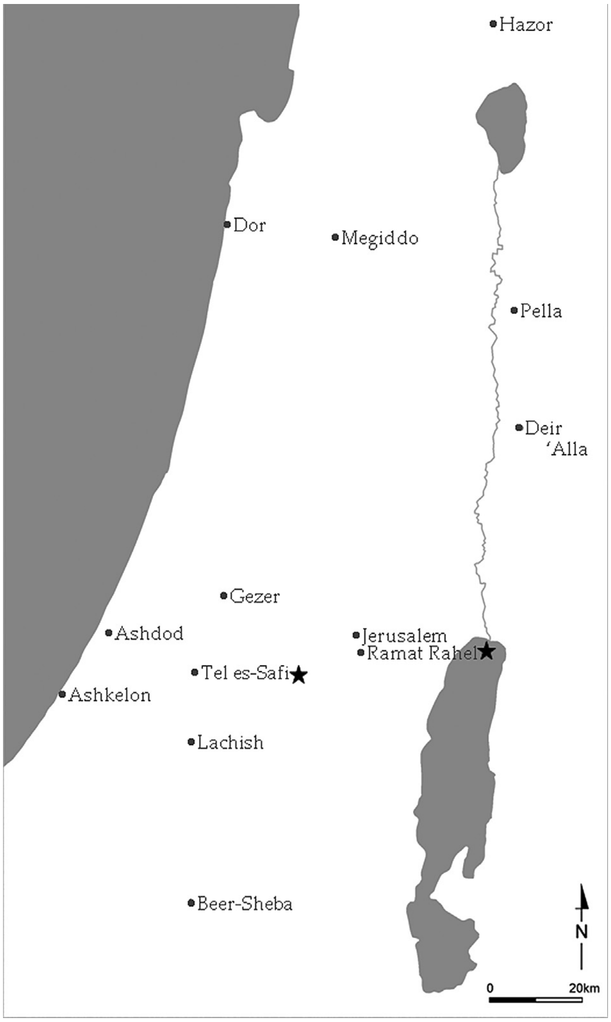

**Fig. 1.** A map of Israel showing the sites from which ceramic samples were collected (marked with a star) relative to other major archaeological sites in the area.

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