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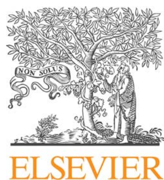

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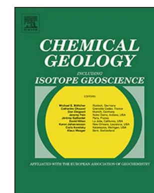

Decontamination of geological samples by gas cluster ion beam etching or ultra violet/ozone

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ABSTRACT

The organic matter within rocks contains chemical and isotopic evidence of its provenance, including information on past and extant life. Such information could further the understanding of life on the early Earth and yield evidence of the existence of past life on Mars. However, the collection of geological samples and subsequent transfer to analytical facilities possibly via long-term storage provides ample opportunity for organic contamination from a variety of sources prior to analysis. Erroneous assignment of organic contamination as authentic indigenous organic material is a significant issue in any geological specimen, but is exacerbated in rocks containing trace levels. This investigation evaluated two decontamination methods for geological samples, namely, the recently developed gas cluster ion beam etching, which supersedes monoatomic sputter etching, and ultra violet/ozone cleaning. Decontamination evaluation involved removal of intentionally applied organic contamination applied to basalt which initially possessed only trace levels of indigenous organic material. Pyrolysis-gas chromatography/mass spectrometry, and X-ray photoelectron spectroscopy were used to measure contaminant removal. Both techniques are suitable for removing organic contamination during the preparation of geological samples.

1. Introduction

Analysis of organic matter embedded in rocks can provide information regarding its origins. Of particular importance are molecular biomarkers which are linked to past or present biological activity (Eglinton, 1964; Eigenbrode, 2007; Summons et al., 2007). Biomarkers can provide insights into the identity and processes associated with fossils on the Earth (Brocks et al., 1999; Briggs and Summons, 2014) and could potentially provide evidence for past life on Mars (Summons et al., 2011). Consequently, it is essential that biomarkers detected are actually indigenous to the host rock in question and are distinguished from those that were subsequently introduced from non-indigenous natural processes or during sample removal, storage, and preparation for analysis (Brocks and Banfield, 2007; Sherman et al., 2007).

Decontamination of acquisition equipment is vital (Eigenbrode et al., 2009) as is the scrupulous decontamination of geological samples after removal from the environment, for example, during the sampling of sectioned drill cores. Chemicals such as chromic acid or organic solvents are frequently employed to clean geological samples but these can be hazardous and risk the deposition of adventitious carbonaceous material. When rocks contain only trace levels of indigenous organic matter (< 100 ppb) unintentional addition of organic matter makes a significant contribution to the net organic inventory, which may be erroneously identified. Furthermore, indigenous organic matter is often found in small and precious fossils and meteorites, which require minimally destructive decontamination protocols. This study tested two methods usually employed in surface cleaning for analysis of semi-conductors in Materials Science. Specifically, the recently developed argon gas cluster ion beam (GCIB) etching, which removes surface contamination more gently than earlier monoatomic etching, and ultra violet ozone (UV/O), to decontaminate the surface layers of geological samples contaminated during acquisition and storage.

1.1. Gas cluster ion beam etching

Monatomic ion beam sputter etching has previously been employed to physically remove surface contamination from semi-conductors (e.g. Czanderna, 2012; Taborelli, 2007) and has even been applied to a tuff

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sample prior to analysis (Preston et al., 2011). However, for this technique, individual high energy ions are propelled up to 20 nm into surfaces which may force surface material deeper into the sample, thus mixing any surface adventitious contamination with any underlying indigenous organic material of interest. Furthermore, the concentrated energy will break chemical bonds, destroying chemical and molecular information. This is problematic for the 1–10 nm and 1 nm analysis depths, encompassed by surface analytical techniques such as X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Spectroscopy (ToF SIMS) respectively. ToF SIMS is unable to make accurate quantitative measurements to the level required in this study, without the extensive use of reference authentic standards. Therefore, its use was outside the scope of this quantitative study (Briggs and Grant, 2003; Garrison and Postawa, 2013; Postawa, 2004; Rabbani et al., 2011).

The drawbacks with monatomic sputtering have been mitigated by the recently developed argon gas cluster ion beam (GCIB), which creates a beam consisting of clusters of 1000 argon atoms with a single charge, rather than individual argon ions. The energy is thus distributed across all atoms in the cluster therefore greatly reducing the damage depth created by the atoms in the cluster. Consequently, a crater only a few nm deep in the surface of the sample can be created. The depth of the crater is dependent upon on several factors such as the cluster size, the impact energy and the composition of the target sample. This process removes material in the predefined area exposed to the gas clusters (Cheng and Winograd, 2006; Cheng et al., 2006; Yamada et al., 2001). Damage to chemical bonds in organic compounds caused by GCIB is minimal and, therefore, the chemical states of the target material are available for analysis (Barlow et al., 2014; Counsell et al., 2014; Mahoney, 2010; Miyayama et al., 2010; Shard et al., 2012; Shard et al., 2015; Winograd et al., 2006; Yamada et al., 2001).

GCIB is routinely used to clean semiconductors, but it has been recently applied for decontaminating geological samples, prior to the surface analysis of paleobiological and astrobiological significance (Sano et al., 2016). Here GCIB has been used for the first time within an XPS instrument in order to rigorously evaluate its effectiveness at decontamination.

1.2. Ultra violet light and ozone (UV/O) cleaning

Ultraviolet-ozone (UV/O) cleaning, utilises a combination of UV light to photolytically breakdown organic material, and ozone that fully oxidises the breakdown products (Vig, 1985) to decontaminate the entire surface of a sample. UV/O has been used for many cleaning applications (Vig, 1985; Cumpson and Seah, 1996) including olivine and feldspar geological samples, albeit without rigorous evaluation (Nugent et al., 1998; Hausrath et al., 2008). Here UV/O decontamination of basalt was evaluated using XPS and pyrolysis-gas chromatography mass spectrometry (py-GCMS), an analytical technique which identifies molecular information in organic compounds from a bulk sample e.g. (Mason et al., 2009).

1.3. Intentional contamination for evaluating decontamination methods

The strategy adopted in this study was to use WD40 to deliberately contaminate a low indigenous organic carbon basalt sample. WD40, a commercially available silicon lubricant, commonly used to clean and lubricate cutting tools, was previously employed to evaluate the decontamination of silicon wafers by UV/O cleaning (Cumpson and Sano, 2013). The organic components in WD40 that evaporate at temperatures < 100 °C at atmospheric pressure, will evaporate when they are exposed to the ultra-high vacuum of the XPS instrument analysis chamber, leaving a residue of low volatility high molecular weight organic compounds. So, although WD40 is not a contaminant encountered in standard geological investigations, in chemical terms, its residue represents a particularly difficult contaminant to remove compared to, for example, a pure low molecular weight hydrocarbon. Additionally, the levels of intentional contamination used in this study were in excess of what might be encountered during geological sample preparation and storage. This intentional contamination therefore provides a greater challenge for both GCIB etching and UV/O cleaning than would be anticipated in typical investigations acting as a 'worst case scenario'. The decontamination efficiency was determined by measuring the decrease in the carbon concentration relative to those of the other elements which constitute the parent rock.

2. Methods

2.1. Sample acquisition, preparation, storage and intentional contamination

The Whin Sill is a 295 Ma tholeiitic quartz dolerite intrusion in northern England, (Fitch, 1967; Liss et al., 2004) which contains trace amounts of indigenous organic carbon readily distinguishable from the increased carbon concentrations resulting from intentional contamination by WD40. A ~1000 g piece of basalt was removed from exposed coastal Whin Sill (WSB) at Craster, Northumberland, UK, (N55° 28.427′ 001 35. 577′ W). The WSB emplaced in Carboniferous strata was exposed by glacial erosion approximately 17,000 years ago (Bateman et al., 2015; Goulty, 2005). Potentially, organic material dissolved in water could be absorbed, then deposited into the surface of rock, to depths greater than those which could be removed using the methods described here. Accordingly, the outer 5–10 mm environment exposed surface was trimmed from the parent sample, revealing un-weathered internal surfaces of basalt, which were then trimmed to ~10 mm × 10 mm × 5 mm pieces, mimicking the acquisition of rock from sectioned core samples. Cutting was carried out using a Norton Clipper power saw and nitrile gloves were worn at all times. Trimmed pieces were handled with flamed forceps, before storage in glass vials sealed with Al foil cleaned by sonication for 30 min in dichloromethane and allowed to dry and closed under screw top lids. Vials were orientated upright during storage and transport, to prevent these 'as received' samples (designated WSB_AR) inadvertently contacting the foil seals.

The faces of WSB_AR samples were photographed to record which face of the basalt piece had been intentionally contaminated. A section of absorbent paper was sprayed with WD40, saturating the paper, then a piece of trimmed basalt was lightly pressed onto the paper for 10 s. These 'intentionally contaminated' pieces (designated as WSB_IC) were then air dried (10 min) and stored in the same way as WSB_AR.

2.2. Decontamination by GCIB etching

Samples were decontaminated within 4 h of intentional contamination using GCIB etching then evaluated using XPS. The GCIB etching was conducted on WSB_AR in triplicate, and on WSB_IC using a protocol adapted from Barlow et al. (2014). The GCIB source was a Thermo Scientific™ MAGCIS™ gun within the XPS instrument, operated at 4 keV generating a broad, semi-log distribution of argon cluster sizes centred on 1000 atoms per cluster at an input pressure of 4 bar. Neutral atoms are not expected to escape from the MAGCIS™ due to a 2° bend in the ion optics. Furthermore, argon clusters with multiple charges were not expected to be stable enough to emerge from the source. The beam current was stable around 20 nA ± 2 nA (as measured at the sample plate within the instrument). An Ar GCIB raster of 1 mm × 2 mm was used, with an X-ray spot size of 200 × 400 μm, providing a gap of 0.4 mm and 0.8 mm between the perimeter of the GCIB etch area and the perimeter of the XPS analysis, i.e. comfortably within the area of the sputter crater. Z-axis depth profiles were obtained by GCIB sputter etching with survey XPS analyses immediately conducted between each sputter etch treatment. The GCIB was rastered over the WSB_IC sample in 19 × 10 s increments for a total of 190 s. Additionally, The WSB_AR samples were etched in 4 × 30 s intervals for a total of 120 s, on three

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