Title: Exploring Graphene Oxide in Environmentally Altered Graphite: A Link Between Chemistry and Archaeology

Abstract:

Graphene oxide (GO) has drawn a great deal of attention, in a laboratory setting, due to its ability to stay suspended in water more easily for solution processing of graphene. In an outdoor setting, it is possible that GO is formed as graphite degrades over time in charred carbon-rich materials such as archaeological charcoal. This GO could be used as a valuable source for radiocarbon dating because its carbon would have the same age as the graphitic carbon that is traditionally extracted for dating. Before radiocarbon dating, graphitic samples are cleaned using a series of strong acid and base treatments to remove contaminants. However, this cleaning procedure can break down some graphite-based samples, leaving no graphite for 14C dating. In those situations, we suspect that GO is cleaned away along with the unwanted contaminants. Our studies are the first to investigate whether GO exists in archaeological charcoal and if it can be separated effectively from contaminants. These findings will be particularly useful for chemists and environmental scientists who work with natural sources of graphite in which oxidized graphenic materials may be present.

Here, we show that a mixture of graphite, GO, and fluorescent carbon-based materials can be present in archaeological charcoal. We also develop a straightforward protocol that separates a simple test case of a lab-prepared mixture of these three components. Our results help to explain why a significant amount of archaeological charcoal is sometimes lost during aqueous cleaning treatments at different pH values.

The fluorescent carbon-based materials described above could originate from either the original graphite (in the form of highly oxidized pieces, called oxidative debris (OD)) or from contaminants (such as humic acid (HA)). The fluorescent materials stay suspended in alkaline aqueous solutions. Although UV-Vis data of base-treated archaeological charcoal shows evidence of oxidized carbon, it is not informative enough to study a mixture of oxidized graphite, OD, and HA. Therefore, we monitor UV absorption at specific wavelengths as a function of retention time using size exclusion chromatography. Our results demonstrate that distinguishing oxidized graphite, OD, and HA from each other is very challenging. Based on SEC results, we identify materials in archaeological charcoal that have similar UV excitation responses and similar retention time (size) to a common HA standard, as well as other components with similar UV excitation responses at longer retention times (smaller sizes).