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Short communication

Cambrian trilobites as archives for Anthropocene biomarkers and other chemical compounds

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ABSTRACT

This study examined well-preserved trilobite fossils from the middle-Cambrian (~507 million years ago) Wheeler Shale of Utah to determine the proportion of original marine biomarkers compared to later chemical overprints. Using a technique to characterize multiple biomarkers simultaneously, the fossils revealed more about modern terrestrial ecosystems and anthropogenic influence than they did about early Paleozoic oceans. Plasticizers, flame retardants, petroleum byproducts, and insect repellent comprised up to 96% of all compounds present in the trilobite exoskeletons, whereas the rest included biomarkers indicating algae, vascular plants (e.g., conifers), and biomass burning inputs. Importantly, contamination occurred despite measures taken to minimize it, highlighting the pervasiveness of anthropogenic contaminants in fossils. These compounds provide invaluable data concerning regional anthropogenic alteration, even though scientific papers usually do not report the types and diversity of contaminants. Scientists must therefore record the composition and amounts of these chemical contaminants because the potential for overprinting could also bias other geochemical measurements, such as stable carbon isotopes, highlighting the need to constrain the sources of contamination within samples. Although the middle Cambrian fossils appear to be excellently preserved, their chemical composition is mainly an Anthropocene overprint.

1. Introduction

The Anthropocene is mostly characterized by alteration to the Earth's surface, such as tropical deforestation (Mahli et al., 2014), urbanization (Steffen et al., 2007) and their resultant effects on biodiversity loss and climate change (Karl and Trenberth, 2003; Dirzo et al., 2014). However, the subsurface effects of physical anthropogenic influence, such as drilling and mining as forms of human bioturbation ('anthroturbation'), are just beginning to be explored (Zalasiewicz et al., 2014). In addition to subsurface physical alteration, we show that anthropogenic compounds can greatly affect the preservation of chemical biomarkers of ancient fossils that were buried in rock for ~507 million years.

Molecular biomarkers are a widely adopted biogeochemical tool to explore ancient communities in the fossil record (Brocks and Summons, 2005; Brocks et al., 2005; Grice et al., 2005; Olcott et al., 2005; Brocks and Schaeffer, 2008; Pawlowska et al., 2012; O'Malley et al., 2013). Even if well preserved for millions of years, rocks and fossils collected at or near the surface are exposed to modern compounds that can overprint the original chemical fossil record (Wischmann et al., 2002; Rasmussen et al., 2008; French et al., 2015). Those compounds are usually not reported in geological or anthropological analyses, but here we highlight the importance of these contaminants as markers for geographic anthropogenic change, both of the subsurface and through potential collection and handling bias.

A set of excellently-preserved middle Cambrian trilobites (~507 Ma) from the Wheeler Shale, Utah, were examined using a multibiomarker approach which allowed for a comprehensive characterization of the biomarker record (Simoneit et al., 2014). This method reveals a number of chemical compounds indicative of ecosystems, unlike a priori targeting a specific biomarker chemical class (e.g., *n*-alkanes or fatty acids). While originally

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looking for Cambrian biomarkers, we found that the trilobites were extensively overprinted by mostly anthropogenic chemical compounds. Although the fossils were well preserved based on morphology, their chemical record was not. It is important that these chemical compounds are reported in Earth system analyses, as they provide a window into the subterranean effects of the Anthropocene that can be compared across geographic regions. In addition, contamination introduced during sample collection and handling could affect bulk carbon values, resulting in a biased interpretation of the record.

2. Materials and methods

Trilobites were quarried commercially from shale beds that once represented a middle Cambrian ocean, now known as the Wheeler Shale of the Great Basin, Utah (USA). Fossils were from the Wheeler Formation, which was deposited within the House Range Embayment; the stratigraphic position represents the *Bolaspidella* polymerid trilobite zone of the mid-middle Cambrian (see Brett et al., 2009). Trilobites were collected by West Desert Collectors and Terra Trilobites, Delta, Utah, from rock depths up to five meters, using two methods: (1) typical geological collecting techniques (hereafter referred to as the "unprotected" set) and (2) protected from plastics during extraction, shipping and handling (the "protected" set). We kept each data set separate to compare the difference in the two collection techniques. The ptychopariid trilobite, *Elrathia kingii,* and the much smaller agnostid trilobite, *Peronopsis interstricta,* were used for analysis (Fig. 1). Petrographically, all had well preserved and complete calcite ($CaCO_3$) exoskeletons (~10 μm in thickness). Two each of protected and unprotected *Elrathia* were powdered, extracted using solvents and derivatized for molecular composition analysis (discussed below). Because *Peronopsis* is much smaller than *Elrathia*, two sets of eight specimens were powdered to yield two samples from the unprotected specimens; eight additional *Peronopsis* were powdered from the protected specimens, yielding one sample. Two sediment samples from the unprotected Wheeler Shale and sediment associated with each species from the protected set were also powdered for analysis. The trilobites and sediment were then prepared for biomarker analysis by gas chromatography–mass spectrometry (GC–MS; Supplementary Methods).

The GC–MS analysis yielded a profile of individual biomarkers present in each sample, following a multibiomarker method (Medeiros and Simoneit, 2007, 2008a,b; Simoneit et al., 2014). This method allows for a simultaneous characterization of the different chemical classes spanning a wide range of polarities without a need to isolate certain chemical classes before analysis (Supplementary Table 1 shows recoveries for major individual compounds found in this study).

3. Results and discussion

The ancient trilobites had extensive chemical overprints from non-Cambrian natural biomarkers and anthropogenic chemical compounds. Specimens contained a higher percentage of biogenic compounds among protected (59.2%) than unprotected (23.6%) exoskeletons and sediments, and anthropogenic concentrations were likewise lower among protected specimens

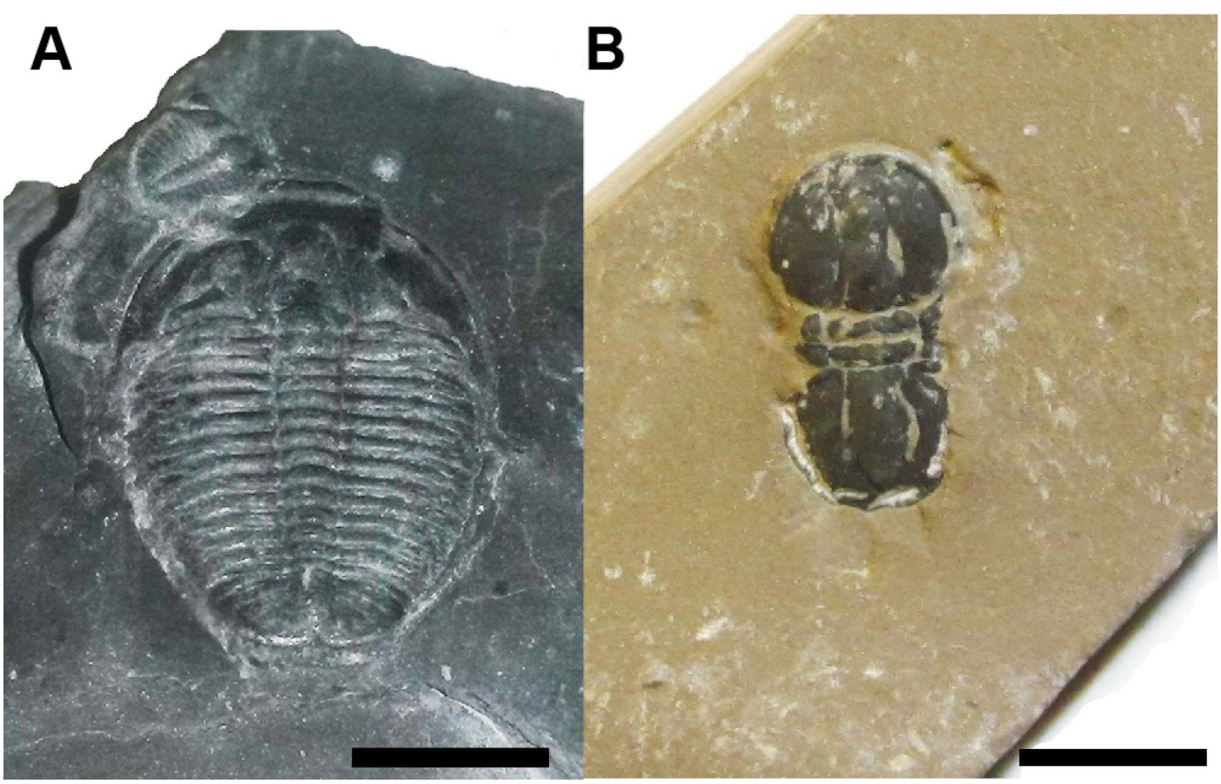

Fig. 1. Common Wheeler Shale trilobites used for multibiomarker analyses. (A) The ptychoparid *Elrathia kingii*; (B) the agnostid *Peronopsis*. Scale bar = 0.5 cm.