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Potential for impact glass to preserve microbial metabolism

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ABSTRACT

Here we provide the first high-resolution geochemical evidence for microbial metabolism to be preserved in impact-generated materials. This study is unique as not only do we merge complimentary analytical techniques such as high-resolution spectromicroscopy to assess the biogenicity of tubules in impact glasses, but we compare these results to those from co-occurring abiotic quench crystallites as an intrinsic negative control. Scanning transmission X-ray microscopy (STXM) near edge X-ray absorption fine structure spectroscopy (NEXAFS) at the Fe L_3- and C K-edges revealed iron speciation patterns and organic C associated with tubular features in the impact glass. The high spatial resolution of STXM combined with NEXAFS allowed organic carbon to be localized to the tubule features. The fine energy resolution of NEXAFS allowed for unique populations of organic carbon to be spectrally differentiated between the tubule features and the matrix. The distinct and systematic variation in iron redox states observed is consistent with microbially mediated dissimilatory iron reduction. The Ries tubules comprise the first trace fossil preserved in a substrate unique to the impact process, thus illustrating the potential for microbial metabolism to be preserved in impact materials.

1. Introduction

Biological activity has undoubtedly had a significant effect on the terrestrial geochemical rock record for at least the past two billion years. Biogeochemical interactions on Earth give rise to distinct sets of biosignatures, features that can be attributed uniquely to biological phenomena, used to interpret the temporal and spatial extent of life on Earth and set a precedent for the interpretation of putative biosignatures beyond Earth. Meteorite impact structures have become paramount in the search for habitable environments on Mars (e.g. Grotzinger et al., 2012). Impact glass, a ubiquitous product of impact events that forms via the quenching of molten material, has recently been shown to preserve evidence of life (Sapers et al., 2014; Schultz et al., 2014). Impact glasses are more geochemically heterogeneous than volcanic glasses as a result of the different melting processes and this results in a greater potential metabolic diversity in colonizing microorganisms. Studies of impact glasses hosted within glass-bearing breccias of the Ries impact structure, Germany (Fig. 1), have revealed the presence of conspicuous tubular structures with complex morphologies associated with organic material suggesting a biogenic origin (Fig. 2a; Sapers et al., 2014). While the Ries tubules preserve evidence of post-impact colonization, Schultz et al. (2014), demonstrate the potential for pre-impact biological material to be preserved in impact glass. Impact glass from the Argentinian loessoid sediments have been shown to encapsulate plant matter, preserving macro- to micro-scale morphological biosignatures in addition to a variety of complex organic molecules (Schutz et al., 2014). Evidence for the preservation of microbial metabolism constitutes a third biosignature preserved in impact glass and is significant not only demonstrating the presence life, but furthermore, potentially identifies a specific life process indicating microorganisms were actively utilizing impact-generated substrates to acquire energy for growth. The recent spectral identification of impact glass on Mars (Cannon and Mustard, 2015) underscores the importance of investigating the biogeochemical potential for impact glass to both host and preserved evidence of biological activity.

Establishing the biogenicity of a putative biosignature such as a potential trace fossil is notoriously difficult (e.g., Brasier et al., 2002) and requires multiple lines of evidence and complemen-

Abbreviations: DIRM, dissimilatory iron reducing microorganism(s); EPU, elliptically polarizing undulator; FIB, focused ion beam; FTIR, Fourier transform infrared spectroscopy; NEXAFS, near-edge X-ray absorption fine structure; STXM, scanning transmission X-ray microscopy.

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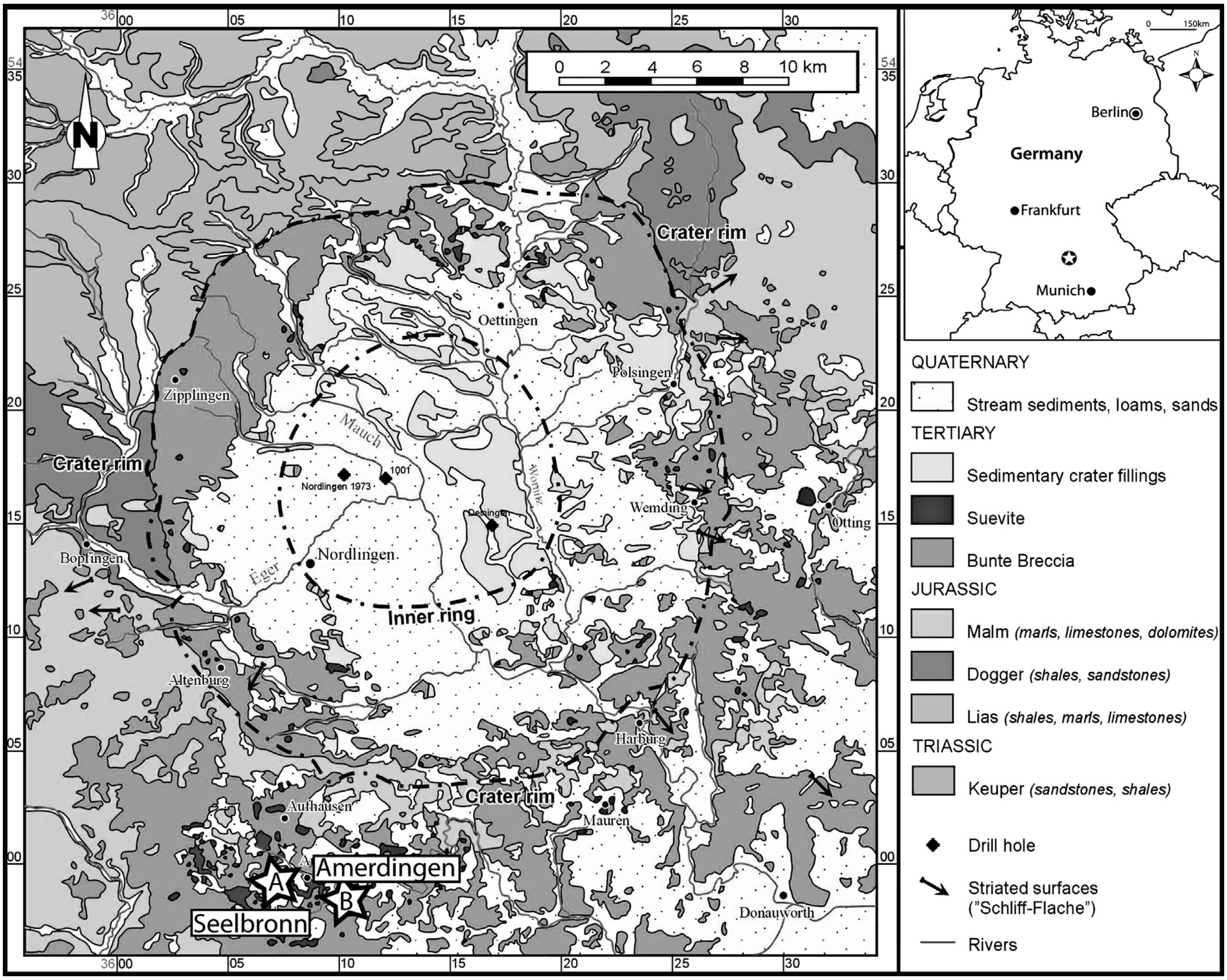

Fig. 1. Geological Map of the Ries impact structure showing sample locations. Samples of glass-bearing breccia (suevite) A1 and A2 were obtained from Seelbronn and samples B1 and B2 from Amerdingen. Modified from Osinski (2003).

tary data sets consistent with a biological origin while discounting abiotic formation mechanisms (e.g., McLoughlin et al., 2007; McLoughlin et al., 2010). This is especially problematic when dealing with ancient systems, systems with very little to no organic matter, such as the tubules in the Ries impact glasses, or systems with limited exposure and access, such as the remote exploration of Gale Crater by the Curiosity Rover and Mars Science Laboratory (MSL) team (Grotzinger et al., 2012). Without abundant organic matter such as nucleic acids and proteins, *in situ* detection of biological material is not possible and the biogenicity of such features is often questioned (e.g. Gibson et al., 2001). Scanning transmission X-ray microscopy (STXM) near edge X-ray absorption fine structure spectroscopy (NEXAFS), described below, has been used to analyze putative bioalteration textures in natural glass samples with low concentrations of organic matter (Benzerara et al., 2007).

2. Synchrotron spectromicroscopy

The identification of organic compounds present at low concentrations at high spatial resolution in natural materials is particularly challenging. The extremely high chemical specificity (spectral resolution) of near edge X-ray absorption fine structure spectroscopy (NEXAFS) and the high spatial resolution of scanning transmission X-ray microscopy (STXM) renders synchrotron based spectromicroscopy an unprecedented microanalysis tool (Myneni, 2002; Urquhart and Ade, 2002). NEXAFS spectromicroscopy can be used for the analysis of complex organic materials where the organic components are well understood and for which spectroscopic reference spectra can be obtained (Urquhart et al., 1999). NEXAFS carbon spectromicroscopy allows for direct chemical characterization of untreated natural samples at nanometer resolution. NEXAFS has been successfully used to identify organic components in many diverse natural samples including extra-terrestrial material (Wirick et al., 2009), fossilized material (Boyce et al., 2002), and from within bioturbation of basaltic glass (Benzerara et al., 2007). NEXAFS spectroscopy can be used to speciate and identify the molecular configuration of an atom of interest as the absolute-edge energy and near-edge fine structure oscillations are dependent on the oxidation state and the average local bonding geometry respectively of the absorbing atom (e.g. Myneni, 2002).

3. The Ries impact structure

The mid – Miocene Ries impact structure located in southern Germany is arguably one of the most accessible and best-preserved terrestrial impact structures (Fig. 1; see Engelhardt, 1990; Pohl et al., 1977 for reviews). $^{40}Ar/^{39}Ar$ laser-probe dating of impact melt particles constrains the age of the Ries impact structure to $14.6 + 0.2$ Ma (Buchner et al., 2010). Ries is a complex crater with a diameter of ∼24 km (Fig. 1; Pohl et al., 1977). Detailed studies have characterized the impact-generated