



# Isotopic evidence for microbial production and consumption of methane in the upper continental crust throughout the Phanerozoic eon



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## ABSTRACT

Microorganisms produce and consume methane in terrestrial surface environments, sea sediments and, as indicated by recent discoveries, in fractured crystalline bedrock. These processes in the crystalline bedrock remain, however, unexplored both in terms of mechanisms and spatiotemporal distribution. Here we have studied these processes via a multi-method approach including microscale analysis of the stable isotope compositions of calcite and pyrite precipitated in bedrock fractures in the upper crust (down to 1.7 km) at three sites on the Baltic Shield. Microbial processes have caused an intriguing variability of the carbon isotopes in the calcites at all sites, with  $\delta^{13}\text{C}$  spanning as much as  $-93.1\text{‰}$  (related to anaerobic oxidation of methane) to  $+36.5\text{‰}$  (related to methanogenesis). Spatiotemporal coupling between the stable isotope measurements and radiometric age determinations (micro-scale dating using new high-spatial methods: LA-ICP-MS U–Pb for calcite and Rb–Sr for calcite and co-genetic adularia) enabled unprecedented direct timing constraints of the microbial processes to several periods throughout the Phanerozoic eon, dating back to Devonian times. These events have featured variable fluid salinities and temperatures as shown by fluid inclusions in the calcite; dominantly 70–85 °C brines in the Paleozoic and lower temperatures ( $<50\text{--}62\text{ °C}$ ) and salinities in the Mesozoic. Preserved organic compounds, including plant signatures, within the calcite crystals mark the influence of organic matter in descending surficial fluids on the microbial processes in the fracture system, thus linking processes in the deep and surficial biosphere. These findings substantially extend the recognized temporal and spatial range for production and consumption of methane within the upper continental crust.

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## 1. Introduction

Microbial anaerobic oxidation of methane (AOM) in a variety of settings, such as marine sediments (Knittel and Boetius, 2009), the deep seafloor biosphere (Inagaki et al., 2015;

Roussel et al., 2008), fresh water wetlands (Segarra et al., 2015) and at seeps, has been suggested to occur by a syntrophic two-membered microbial consortium, consisting of: 1) anaerobic methanotroph (ANME) *archaea*; and 2) sulfate reducing bacteria (SRB) (Michaelis et al., 2002). This phenomenon occurs at the sulfate–methane transition zone (SMTZ), a discrete depth horizon where sulfate-rich water mixes with deeper-seated methane (Knittel and Boetius, 2009), and frequently results in precipitation of calcite and pyrite from the dissolved bicarbonate and sulfide produced during AOM (Campbell et al., 2002; Peckmann and Thiel, 2004). Methane generally has carbon isotope values ( $^{13}\text{C}/^{12}\text{C}$  expressed as  $\delta^{13}\text{C}$ ) that are light (depleted in  $^{13}\text{C}$ ), especially when it

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is microbial (Whiticar, 1999), although significant  $^{13}\text{C}$ -depletion has also been shown for abiotic methane of hydrothermal origin (McCullom et al., 2010), and hence, the related authigenic calcite is also commonly  $^{13}\text{C}$ -depleted (Campbell et al., 2002; Peckmann and Thiel, 2004; Schrag et al., 2013). This calcite is therefore a frequently used tracer for AOM, in addition to diagnostic biomarkers of ANME and their SRB partner (Niemann and Elvert, 2008). Reports of fossil AOM from numerous sedimentary settings, mostly Cenozoic and rarely Mesozoic/Paleozoic (Peckmann and Thiel, 2004), show that microbial oxidation have decreased the contribution of this greenhouse gas to the surface systems and atmosphere over geological eras.

In the respect of microbial methane production and consumption over Phanerozoic time scales, the vast continental crust, dominated by fractured Precambrian crystalline basement, has largely been neglected. This continental subsurface system has a total estimated biomass corresponding to up to almost 20% of the Earth's total (McMahon and Parnell, 2014). Pioneering investigations within the last decades confirm that microorganisms indeed thrive in this oligotrophic fracture environment (Pedersen, 1997). Although microbial cell densities in water filled fractures are very low (Wu et al., 2016), the vast area and surprisingly high metabolic activities (Onstott et al., 2014) result in microbial mediated redox transitions that significantly influence global carbon and energy fluxes (McMahon and Parnell, 2014). However, the knowledge about ancient life in this vast and difficult-to-reach environment is still very scarce. Basically, fractured crystalline rocks are overall untapped archives for ancient organic processes and materials (Peters et al., 2016).

The presence of abiotic methane deep within fractured crystalline rocks is well known (Sherwood Lollar et al., 2008), and recent observations of highly  $^{13}\text{C}$ -depleted carbonates at Laxemar, Sweden ( $\delta^{13}\text{C}$  as light as  $-125\%$  V-PDB, Drake et al., 2015) and at Olkiluoto, Finland (as light as  $-53.8\%$ , Sahlstedt et al., 2016) have shown that methane has been oxidised by microorganisms at several hundred meters depth in the Precambrian continental crust. These carbonates have been anticipated to be relatively recently formed ( $<10$  Ma) (Drake et al., 2015), but no precise dating constraints have yet been presented. Ongoing AOM is anticipated at these sites by contrasting depth trends of methane and sulfate (Drake et al., 2015; Pedersen et al., 2008, 2014). Although the knowledge of hydrogeochemical and biogeochemical (Drake et al., 2015; Sahlstedt et al., 2016) temporal fluctuations in deep granitoid fracture systems have been significantly improved during recent years by application of microscale isotope techniques, the AOM process in this setting is still largely uncharacterised in terms of mechanisms and unknown in terms of spatiotemporal extent.

The aim of the study was to decipher whether the recently discovered and young ( $<10$  Ma) AOM- and methanogenesis-processes in fractured bedrock (Drake et al., 2015) have been widespread in space and time. The spatial distribution has been assessed by extensive new micro-analytical stable isotope investigations of minerals from several Precambrian crystalline rock sites over large depth range (0–1700 m), and the temporal extent has been targeted by utilizing new dating techniques with high spatial resolution and by focusing on minerals of several generations, indicatively formed in the Paleozoic era (or later) (Drake and Tullborg, 2009). These new isotope and geochronological analyses have been combined with comprehensive characterisation of biomarkers (and fossilised microorganisms) and fluid inclusions within the calcites, with an aim to decipher the fluid salinity and temperature as well as the origin of nutrient sources related to methane formation and consumption processes.

## 2. Materials and methods

### 2.1. Materials and sites

Samples were collected from boreholes at three sites dominated by Proterozoic crystalline rocks. These are Forsmark (rock crystallization age 1.89–1.86 Ga), Göttemar (1.44 Ga) and Laxemar (1.80 Ga, including also subareas Äspö and Simpevarp) in Sweden (Fig. S1). Samples of calcite (and pyrite) were taken from dominantly open, but also semi-open and sealed fractures from 39 cored boreholes, one outcrop and one quarry. Paragenetic minerals include fluorite, adularia K-feldspar, quartz and asphaltite (Figs. 1 and S2).

### 2.2. Microscale stable isotope analysis

Following sample characterisation and mineral identification carried out directly on the uncoated fracture surfaces using a Hitachi S-3400N SEM equipped with an integrated energy dispersive spectroscopy (EDS) system under low-vacuum conditions, calcite and pyrite crystals were mounted in epoxy, polished to expose crystal cross-sections and examined with SEM to trace zonations. Intra-crystal SIMS-analysis (10  $\mu\text{m}$  lateral beam dimension, 1–2  $\mu\text{m}$  depth dimension) of carbon, oxygen and sulfur isotopes were performed on a Cameca IMS1280 ion microprobe. Analytical transects of up to ten analyses were made within the crystals. In total 2465 analyses were made in calcite for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in calcite and 40 for  $\delta^{34}\text{S}$  of pyrite in samples with AOM-signature in the calcites. Settings follow those described in Drake et al. (2015). Influence of organic carbon was avoided in the SIMS-analyses by careful spot placement to areas in the crystals without micro-fractures or inclusions. The uncertainty associated with potential organic inclusions and matrix composition is therefore considered to be insignificant compared to the isotopic variations.

Calcite results are reported as per mil ( $\%$ )  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  based on the Pee Dee Belemnite (V-PDB)-standard value. Several analytical sessions were carried out running blocks of six unknowns bracketed by two standards. Spot transects were made from core to rim within the crystals (summarised in Table 1, with full data in Table S1). Corresponding analytical spots for C and O isotopes were closely placed within the crystals and analysed at separate sessions.

Isotope data from calcite were normalised using 1) Brown Yule Marble ( $\delta^{18}\text{O}$ :  $24.11 \pm 0.13\%$  V-SMOW, converts to  $6.55 \pm 0.13\%$  V-PDB,  $\delta^{13}\text{C}$ :  $-2.28 \pm 0.08\%$  V-PDB, derived from three replicate bulk analyses, J. Craven, Univ. of Edinburgh, pers. comm.), and 2) calcite standard S0161, which comes from a granulite facies marble in the Adirondack Mountains, kindly provided by R.A. Stern (Univ. of Alberta). The values used for IMF correction were determined by conventional stable isotope mass spectrometry at Stockholm University on ten separate pieces, yielding  $\delta^{13}\text{C} = -0.22 \pm 0.11\%$  V-PDB (1 std. dev.) and  $\delta^{18}\text{O} = -5.62 \pm 0.11\%$  V-PDB (1 std. dev.). Precision was  $\delta^{18}\text{O}$ :  $\pm 0.2$ – $0.3\%$  and  $\delta^{13}\text{C}$ :  $\pm 0.4$ – $0.5\%$ .

Pyrite results are reported as per mil ( $\%$ )  $\delta^{34}\text{S}$  based on the Canon Diablo Troilite (V-CDT)-standard value. Blocks of six unknowns were bracketed by two standards (the Ruttan pyrite). Analytical transects of several analyses were made from core to rim in the crystals. Precision was  $\delta^{34}\text{S} \pm 0.13\%$ .

### 2.3. Micro-scale radiometric dating

#### 2.3.1. U–Pb dating

U–Pb geochronology is based on the two decay systems of U to Pb ( $^{238}\text{U}$  to  $^{206}\text{Pb}$  and  $^{235}\text{U}$  to  $^{207}\text{Pb}$ ) and is commonly applied to silicate and phosphate minerals, i.e. zircon and monazite, but can also be applied to carbonate minerals (see Rasbury and Cole, 2009). Using the Laser Ablation Inductively Coupled Plasma

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