Long-term accumulation of microbial methane in the Devonian Siljan impact structure, Sweden

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Summary (Heading in Arial 12pt bold)

At the site of Siljan, in Sweden, a >50 km diameter meteorite impact structure formed ~380 million years ago, and is the largest impact structure in Europe. Previous well-known drilling attempts for deep natural gas are now renewed. Analyses of mineral samples from newly drilled cored boreholes through the crater rim, and from downhole gas samples, reveal widespread evidence for long-term gas accumulation in the crater structure. The methane-dominated gas shows a dominantly microbial geochemical signature, with a minor thermogenic contribution. The isotopic signatures of carbonate in the fractures corroborate this interpretation and speak in favor of *in situ* formation of microbial gas in the fractures. Preserved organic molecules detected within the mineral coatings give additional evidence both for microbial activity in the crater, as molecules specific to certain microorganisms could be detected, but also for microbial biodegradation of shale-derived hydrocarbons, ultimately leading to production of secondary microbial methane at depth, also in the deeper crystalline basement. Signatures of methane oxidation and enhanced gas observations during drilling occur in the contact zone between the Paleozoic sedimentary successions and the deeper bedrock in the crater rim suggesting that methane has accumulated beneath the sediments (cap-rock). Radiometric dating of the mineral coatings show that the microbial gas formation date back at least 80 million years, and thus that it is significantly younger than the impact event. The amounts of gases in the crater structure remain to be quantified.

Theory / Method / Workflow

In the late 1970s and 80s, astrophysicist Thomas Gold put forward controversial theories of significant amounts of mantle-derived methane thought to have ascended the impact-deformed basement at Siljan, and accumulated beneath a shallow cap of carbonate-sealed fractures. Accordingly, from the late 80s, deep exploratory wells were drilled in the central plateau of exhumed Paleoproterozoic granite, but no economic gas quantities could be established and the project was abandoned. High methane concentrations in crystalline rocks are commonly associated with serpentinized ultramafic and graphite-bearing rocks, but at Siljan these rock types are not present and contribution of abiotic methane to the fractured rock aquifers is yet to be proven. In recent years, prospecting for methane was re-initiated here. This time focus was on the fractured crystalline bedrock beneath 200-600 m thick down-faulted Ordovician/Silurian limestones and shales in the ring-like crater depression, and several deep cored boreholes were drilled. Methane accumulations were detected during the drilling campaigns, both in the sedimentary rock and deep within the granite fracture system, but no qualified estimate of total gas volumes has yet been made public.

The thermal maturity of the Ordovician organic-rich shale has reached the initial stage of oil generation, and hydrocarbons have migrated from these more mature sediments into marginally mature sediments. Still, the potential input of thermogenic gas to the deep granite aquifer at Siljan remains elusive. In addition, the potential contribution of microbial methane at Siljan has been completely overlooked. Isotopic and biomarker clues to ancient microbial processes such as methanogenesis and anaerobic oxidation of methane (AOM) with associated sulfate reduction can be preserved within minerals formed in response to these microbial processes. These signatures can remain within the minerals over considerable geological time and advances in high spatial resolution U-Pb geochronology make it possible to gain timing constraints about discrete events of mineral precipitation[1]. Here, these carbon and U-Pb isotopic approaches in combination with analysis of organic compounds and gases are applied to disclose the source and timing of methane accumulation in the Siljan impact structure. See ref.[2] for details and full dataset.

Results, Observations, Conclusions

A dominantly microbial gas fraction is suggested by the light $\delta^{13}C$ values of the methane (-64±2‰,). However, the $C_1/(C_2+C_3)$ values are slightly lower than expected from a pure microbial gas and therefore points to a minor mature thermogenic contribution. This is corroborated by the presence of C_{4+} gases. The heavy $\delta^{13}C_{CO2}$ values (+5-9‰) are typical for microbial methanogenesis through carbonate reduction, thus also supporting a dominantly microbial origin.

For the mineralogical record, significantly ^{13}C-enriched calcite observed in the fractures in limestone ($\delta^{13}C$ values as heavy as +21.5‰) and granite (up to +18.9‰) supports formation following microbial methanogenesis *in situ*, owing to the discrimination that occurs against ^{13}C during methanogenesis, leaving a ^{13}C-rich residual CO_2 behind. Detected fatty acids, particularly the odd chain and branched iC_{15}, aiC_{15}, n-C_{15}, 12Me-C_{16}, aiC_{17}, and 12OH-C_{18} and the n-alcohols and the 1-o-n-hexadecylglycerol preserved within the calcite coatings support microbial activity. U-Pb dating of the fracture calcite suggests that methanogenesis at Siljan lead to precipitation of ^{13}C-rich calcite at several occasions, during fracture reactivation events from 80±5 to 22±2 Ma. The distribution of this calcite marks microbial methanogenesis in the upper 214 m of the fractured crystalline rock in the crater structure (to depths of 620 m) and in the overlying sedimentary rock fractures over a depth span of more than 200 m. Preserved hydrocarbon n-alkane pattern of calcite in bitumen-bearing fractures indicates thermal- and biodegradation of hydrocarbons from the black shale. Light $\delta^{13}C_{calcite}$ values detected at the sediment-granite contact (-52.3‰) reflect anaerobic oxidation of methane and thus propose methane accumulation locally underneath a sedimentary “cap-rock” where enhanced observations of gas where noted during drilling. The 39 Ma age of this calcite suggests long-term methane accumulation. The amounts of gases in the structure remain unquantified, but the microbial origin following utilization of primary shale-derived thermogenic hydrocarbons infers a localization to the rather small volume of rock in spatial relation to the sedimentary-rock dominated ring zone of the crater.

Acknowledgements

Funding: Swedish research council (#2017-05186) and Formas (#2017-00766). Access to drill cores, logs and gas data: AB Igrene. Invitation: Drs. J. Spray and E. Walton.

References

[1]Drake, H. et al. Isotopic evidence for microbial production and consumption of methane in the upper continental crust throughout the Phanerozoic eon. Earth Planet Sci Lett 470, 108-118 (2017). [2]Drake, H., et al. Timing and origin of natural gas accumulation in the Siljan impact structure, Sweden. Nature Comm 10(1): 4736. (2019).

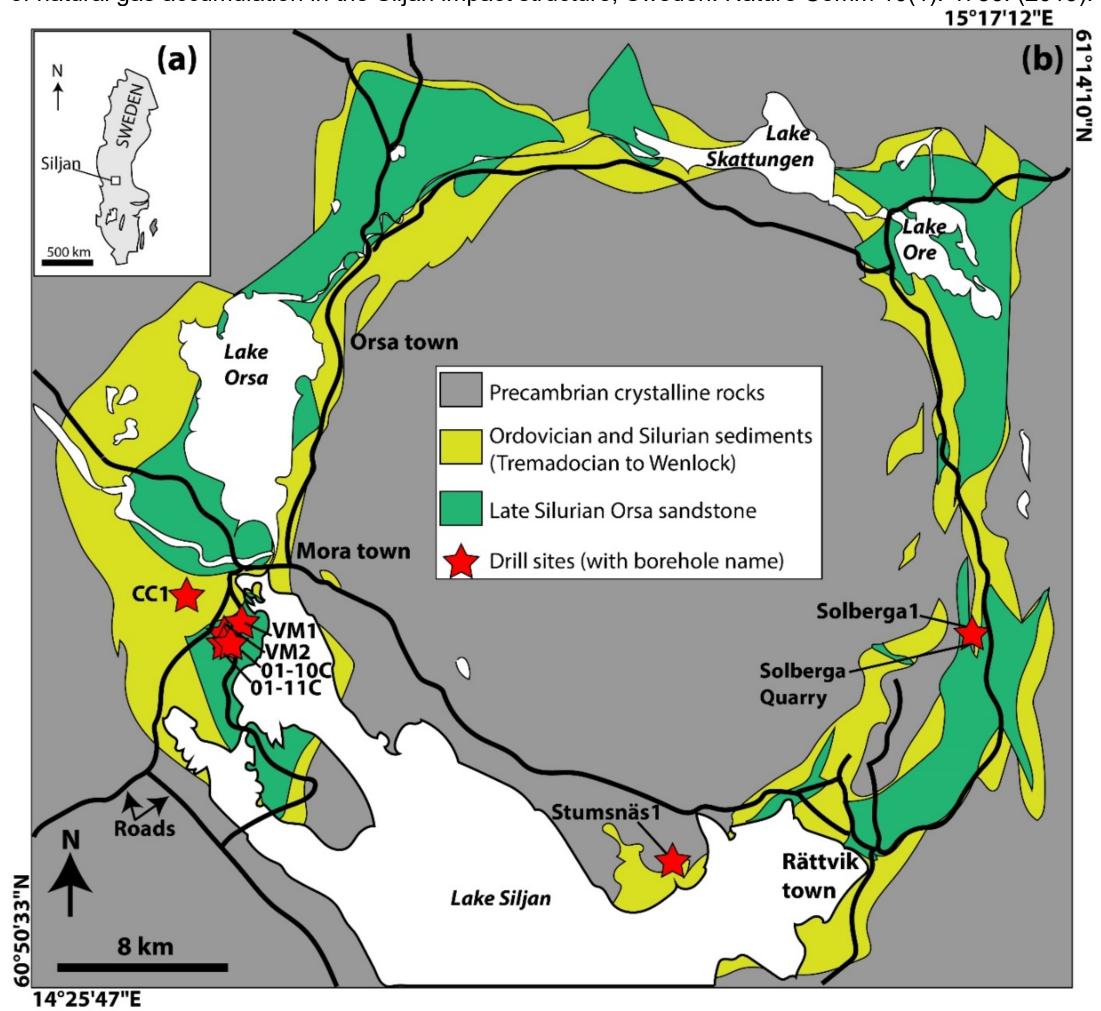

Fig. 1 Maps of the Siljan impact structure and study locations. (a) Map of Sweden with the Siljan area indicated. (b) Geological map of the Siljan impact structure with locations of the cored boreholes sampled for mineral coatings and gases indicated, along with the sedimentary units in the crater depression, towns, lakes (white) and roads (black lines). Modified from2.

Fig. 1 Maps of the Siljan impact structure and study locations. (**a**) Map of Sweden with the Siljan area indicated. (**b**) Geological map of the Siljan impact structure with locations of the cored boreholes and the quarry sampled for mineral coatings indicated, along with the sedimentary units in the crater depression, towns, lakes (white) and roads (black lines). Gas compositions exist from boreholes VM2 and VM5 (located adjacent to VM2). Modified from[2].