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Contact metamorphism, halocarbons, and environmental crises of the past

Henrik Svensen,[A,E] *Norbert Schmidbauer,*[B] *Marco Roscher,*[A] *Frode Stordal*[C] *and Sverre Planke*[A,D]

[A]Physics of Geological Processes (PGP), University of Oslo, PO Box 1048 Blindern, NO-0316 Oslo, Norway.
[B]Norwegian Institute for Air Research, PO Box 100, NO-2027 Kjeller, Norway.
[C]Department of Geosciences, University of Oslo, PO Box 1047 Blindern, NO-0316 Oslo, Norway.
[D]Volcanic Basin Petroleum Research (VBPR), Oslo Research Park, NO-0349 Oslo, Norway.
[E]Corresponding author. Email: hensven@fys.uio.no

Environmental context. What caused the biggest known mass extinction on Earth ~252 million years ago? A possible killer mechanism was the release of specific gases into the atmosphere, which eventually led to destruction of the ozone layer. This is now supported by new laboratory experiments in which ozone-destructing gases were generated when heating rocks from East Siberia (Russia) – reconstructing what happened naturally in Siberia during explosive gas eruptions 252 million years ago.

Abstract. What triggered the largest know mass extinction at the Permian–Triassic boundary 252 million years ago, when 95% of the species in the oceans disappeared? New geological data suggest that eruptions of carbon (CH_4, CO_2) and halocarbon (CH_3Cl and CH_3Br) gases from the vast sedimentary basins of east Siberia could have triggered a period with global warming (5°–10°C) and terrestrial mass extinction. The gases were generated during contact metamorphism of sedimentary rocks around 1200°C hot igneous intrusions. One of the suggested end-Permian extinction mechanisms is the extreme ultraviolet radiation (UV-B) caused by a prolonged destruction of stratospheric ozone induced by the emitted halocarbons. This hypothesis is supported by a new set of experiments, where natural rock salt samples from Siberia were heated to 275°C. Among the gases generated during heating are methyl chloride (CH_3Cl) and methyl bromide (CH_3Br). These findings open up new possibilities for investigating ancient environmental crises.

Introduction

From the geological record we know many episodes of rapid global warming that had severe effects on the environment. Well studied episodes occurred 252 million years ago (Ma) (the end-Permian mass extinction), 200 Ma (the end-Triassic mass extinction), 183 Ma (the Toarcian event), 65 Ma (The KT mass extinction), and 55 Ma (the Paleocene–Eocene thermal maximum (PETM)).[1,2] Although these events differ in duration and severity, they are all characterised by a phase of rapid global warming, typically 5°–10°C, and continental and marine mass extinctions of varying harshness. The only widely accepted extinction mechanism is a meteorite impact at the KT boundary (i.e. the Cretaceous–Paleogene boundary). The trigger and cause of the other events is strongly debated in the geosciences communities and a plethora of hypotheses are currently available. However, all events took place at the same time as the formation of so-called Large Igneous Provinces (LIPs). In 2004 we published a hypothesis explaining the PETM event at 55 Ma by generation and release of carbon gases during contact metamorphism of organic-rich sedimentary rocks around igneous sills offshore Norway.[3] The sills represent the sub-volcanic part of a LIP. More recently, we have suggested that a similar mechanism can be applied to the events at 252, 200, and 183 Ma (Svensen et al.[4,5]), and all are associated with LIPs.

The PETM is probably the best understood event because there are abundant high-quality proxy and geological data available and the continental plates were reasonably close to the present day position. It lasted for ~170 000 years and was characterised by pronounced global warming of 5°–9°C and a mass extinction among marine benthic organisms.[6–9] The intensified greenhouse conditions resulted from the rapid release of several thousand gigatons of ^{12}C-enriched carbon gases to the atmosphere (e.g. Dickens et al.[10]; Zachos et al.[6]; Zeebe et al.[11]). Recent carbon cycle modelling suggests that CO_2 alone, regardless of its source, is insufficient to explain the warming and that methane degassing is a likely mechanism.[11] Degassing of thermogenic methane generated around igneous sill intrusions offshore Norway can explain the volume of carbon needed to trigger global warming.[3] Alternatively, unknown feedback mechanisms contributed significantly to the warming, with a smaller contribution (1°–3.5°C) from carbon gases.[11]

If the link between many of the global events is contact metamorphism of sedimentary rocks, then why is the PETM characterised by global warming and the end-Permian by global warming *and* a major mass extinction? We claim that the main reason is the chemical composition of the heated sedimentary rocks. A key fact is that one of the world's biggest rock salt deposits were intruded by 1200°C igneous sills in east

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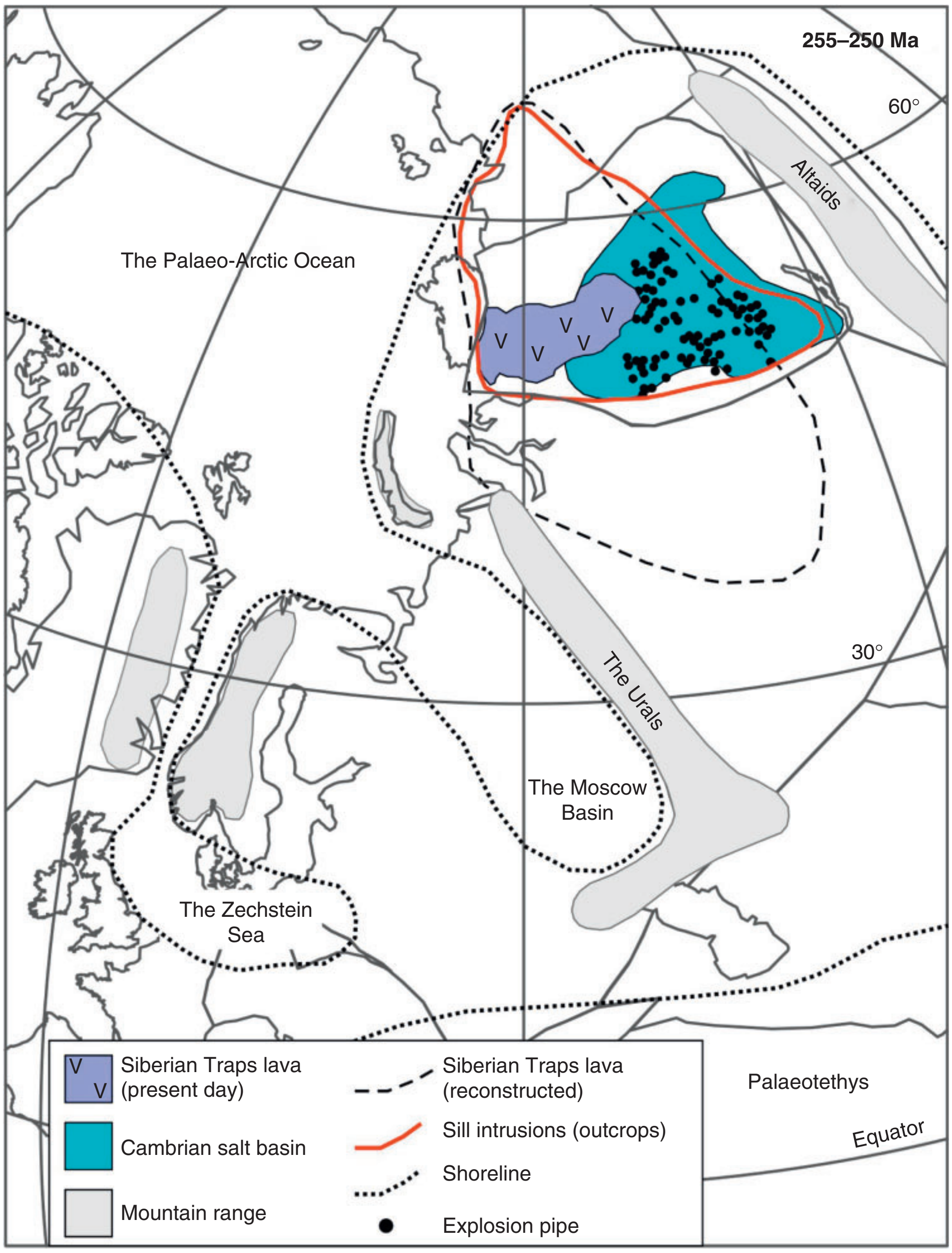

Fig. 1. Reconstructed geography of Eurasia at Permian–Triassic times (~255–250 Ma). The geological boundaries and features of east Siberia are modified from Svensen et al.[4] and Reichow et al.[19]

Siberia at the same time as the end-Permian extinction took place.

The end-Permian event

The end-Permian crisis is the biggest known marine and terrestrial extinction event with loss of 35% of the species on the continents and 95% in the oceans.[1,12] The main stage of the extinction occurred during a relatively short time span of ~200 000 years or less. A global carbon cycle perturbation is recorded by negative $\delta^{13}C$ excursions in marine and terrestrial strata[13] with global warming extending 4–5 million years into to the Triassic (Payne et al.[14]; Payne and Kump[15]).

Amongst the hypotheses for the end-Permian event are H_2S degassing from a stratified ocean followed by ozone layer collapse,[16–18] lava degassing of CO_2 from the Siberian Traps Large Igneous Province (LIP)[1,19–21] possibly also releasing methane from gas hydrates during global warming.[1,22] In addition, it has been proposed that contact metamorphism of coal and other carbonaceous sediments in the Tunguska Basin in Eastern Siberia generated carbon gases that induced global warming[3,4,13,15,23–25] and an accompanying generation and release of halocarbons could have destabilised the ozone layer (Visscher et al.[25]; Beerling et al.[23]; Svensen et al.[4]). In addition, it was recently suggested that degassing of volatile halogenated hydrocarbons from the Zechstein salt basins (see Fig. 1) could have contributed to the ozone depletion.[26] Ozone layer destabilisation is suggested by the discovery of mutated pollen,[25,27] and is thus among the possible killer mechanisms for terrestrial animals and plants via intolerable UV-B levels. Other terrestrial killer mechanisms include atmospheric

Fig. 2. A thick sill intrusion near Bratsk in east Siberia (a). The sill is several hundred metres thick. Person for scale. Rock salt from a drill core at Nepa in east Siberia (b). This core was used for the laboratory heating runs. Close-up of rock salt (nearly pure halite) from the core (c). Contact metamorphic rock salt from the same core (d). The discoloration is due to weathering of sulfides formed as a result of the metamorphism.

hypoxia, whereas anoxia and lowered pH in the oceans could have led to extinction in the oceans.[28,29]

Regardless of what hypothesis you favour, the processes leading to the end-Permian crisis are not well understood, and multiple scenarios and feedback mechanisms likely operated. Nevertheless, the Siberian Traps LIP is a commonly cited trigger. The end-Permian crisis coincide in time with the formation of the Siberian Traps, a volcanic event that covered several million square kilometres of Siberia with kilometre-thick lava over a period of 0.5–1 million years (Bowring et al.[30]; Wignall[1]; Mundil et al.[31]; Kamo et al.[32]). This is shown in Fig. 1 where we have reconstructed the plate configurations for the late Permian and added the extent of the present day lava and sill outcrops and the inferred maximum extent of the lava flows in the early Triassic.

On the way to surface, the lavas in East Siberia passed through a thick pile of sedimentary rocks in the Tunguska Basin. Igneous sills and dykes are abundant throughout the basin (Fig. 1), and form sheets up to 350 m-thick, locally comprising 65% of the basin fill.[33–35] An outcropping sill intrusion from East Siberia is shown in Fig. 2a. The magmatic intrusions had a temperature of ∼1200°C and led to widespread heating (contact metamorphism) of the sedimentary rocks and the generation of carbon gases from disperse organic matter and petroleum accumulations. The Tunguska Basin contains enormous volumes of Cambrian evaporites, with up to 2.5 km-thick sequences of halite-rich strata (Fig. 2b–d), anhydrite, and carbonates in a 2 million-km^2 area (Fig. 1).[36,37] The contact metamorphism led to overpressure within salt-dominated lithologies and the formation of explosion pipes[4,38,39] that released the gases to the atmosphere (Figs 1, 3).

In order to better characterise the gases generated during heating of the sedimentary rocks 252 Ma we collected samples of rock salt in Siberia during field work in 2004 and 2006. Eight samples were heated to 275°C in a GC-MS,[4] as described below, to simulate contact metamorphism. The ultimate goal was to test the hypothesis of ozone-depletion by halocarbon generation (methyl chloride) and degassing to the atmosphere.[25]

How to generate halocarbons from rocks

The rock salt contained petroleum-bearing fluid inclusions, as verified from room temperature extraction after crushing the samples in a sealed chamber (see Svensen et al.[4] for details). In contrast to the room temperature gas composition, halocarbons like methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) were identified in all heating runs. The maximum concentration

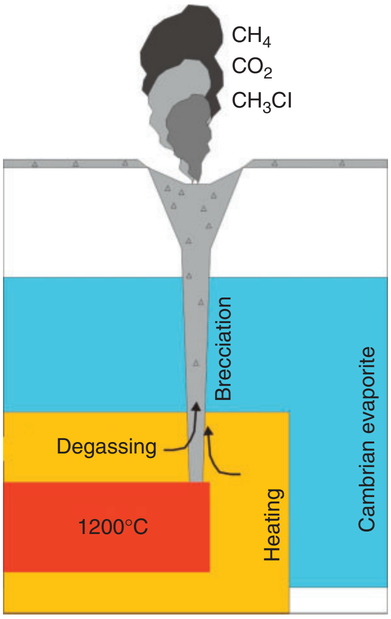

Fig. 3. Schematic cross-section of a pipe structure from the Tunguska Basin in east Siberia. The pipe formed as a result of pressure build-up around a magmatic intrusion at depth (red), and the heating process generated carbon gases and halocarbons from organic matter and petroleum within the thick evaporite deposits (containing halite, anhydrite, and dolomite). The zone of contact metamorphism is shown in orange. The generated gases in the contact aureole were subsequently released to the atmosphere. The sill intrusion would typically be 200 m thick and the crater diameter ∼1.5 km (based on data from Siberia).

of methyl chloride was 161 ng g^{-1} rock and the mass ratio of methyl chloride to methyl bromide was between 6.6 and 58.6 with an average of 17.3 for the eight experiments. Halogenated butane, especially 1-chloro-butane (C_4H_9Cl), was present in considerable amounts (up to 51 ng g^{-1} rock) in most runs as well as 1-bromo-butane (C_4H_9Br). To our knowledge, this is the first time that heating of natural rock samples in the laboratory has generated halocarbons. Previous experiments have solely focussed on biological samples.[40,41] Even though the details about halocarbon formation during our experiments remains poorly understood, we attribute the formation of these molecules to high temperature reactions between hydrocarbon compounds within the fluid inclusions and dissolved chloride from the rock salt. Thus the experiments add to the geological knowledge about what happens when evaporites are heated by igneous sill intrusions.

Halocarbons and the end-Permian ozone layer

Halocarbons like chloromethane are known to be produced and emitted from several natural sources within the Earth's crust. Both methyl and ethyl halides are known from degassing volcanoes along subduction zones,[42] although many of the reported emissions may represent air contamination.[43] In any case, the largest source of abiotic atmospheric CH_3Cl is biomass burning.[44,45]

The present day methyl chloride cycle has implications for understanding halocarbon emissions in deep time and possible halocarbon sources. For instance, the Siberian Traps lavas could not have emitted large quantities of halocarbons if we assume that the current volcanic emissions are low and relevant for the Siberian Traps lavas. Furthermore, recent atmospheric modelling shows that oceanic H_2S release and methane could not have destroyed the end-Permian stratospheric ozone.[46] Because there are no indications of a global wildfire during the end-Permian,[47] additional halocarbon sources must have existed during the end-Permian for the ozone layer destruction hypothesis to explain the terrestrial extinction. Halocarbons from salt pans or soils is a possibility, and the coupling between present day processes and comparable processes during the late Permian is interesting.[26] Still, degassing of halocarbons from east Siberia remains one of the most promising explanations when searching for unique processes behind the end-Permian terrestrial crisis. Violent degassing, as suggested by the pipes in Siberia, makes it likely that the gases passed the otherwise rather undisturbed tropopause and were injected into the stratosphere.

The vast volumes of heated sedimentary rocks in east Siberia during the end-Permian (∼400 000 km^3) implies that even small amounts of generated and released halocarbons per rock unit sum up to enormous volumes. Mass balance calculations suggest that 10 000–30 000 Gt C could have been generated in Siberia, accompanied by 4500–13 000 Gt CH_3Cl.[4] The timescale of release is poorly constrained but is argued to be within a few 10 000 years. The resulting average flux of CH_3Cl is up to 0.3 Gt $year^{-1}$.

Recent atmospheric modelling shows that >1000 Gt of methyl chloride are required to cause significant stratospheric ozone depletion over a 100 000 year time scale, with a resulting flux of ∼0.1 Gt $year^{-1}$.[23] Our results are well within those limits. Furthermore, methyl bromide will escalate the ozone depletion process but has so far not been taken into account. In addition, both sill emplacement and gas eruptions could have taken place as a series of short-term events in which each event would yield a larger flux of halocarbons to the atmosphere. As the adjustment time for ozone in the stratosphere is less than 10 years and UV responds instantaneously, a scenario with rapid degassing in pulses would result in more severe UV stress.

A proxy for disaster?

A main challenge in geosciences today is to get better proxies for environmental changes. Isotope geochemistry of organic matter, microfossils, and minerals from sedimentary Permian–Triassic boundary sections are widely used to obtain proxy data for the atmospheric composition and the carbon cycle. An open question is how to determine the best proxies for environmental changes induced by halocarbons.

How can halocarbon release and ozone depletion 252 Ma be verified, and what traces would extraordinary high concentrations of halocarbons in the atmosphere leave behind? Atmospheric chemistry modelling can certainly provide us with boundary conditions and we know from the geology of East Siberia and the presented experiments that halocarbons and methane were released to the atmosphere. Currently, the best indication that the ozone layer was under attack during the end-Permain comes from pollen. Several publications have documented the presence of mutated pollen in the end-Permian world, and the mutations are attributed to high levels of UV-B radiation.[25,27]

The problem with proxy data is the non-uniqueness with respect to the underlying process, and more work is needed until the ozone-hypothesis is verified. A very promising recent approach is to analyse UV-B sensitive compounds in pollen (*p*-coumaric acid and ferulic acid),[48] but it remains to be tested if this method can be used to construct proxy data for ozone based on pollen as old as the Permian and Triassic.

More work is also needed to explore the halocarbon degassing hypothesis as presented here. New quantitative experiments on rock salt must be conducted in the full temperature range relevant for geological conditions (200°–600°C) and improved pipe degassing scenarios for east Siberia needs to be made, also including gases released from the lava flows.

The geochemistry of extinctions

To summarise, one of the key questions in paleoclimate research is to understand why some environmental crises are characterised by major mass extinctions, whereas others are primarily global warming events (like the PETM). We suggest that rapid release of greenhouse gases together with ozone-depleting compounds (halocarbons) is a possible explanation. We stress that the chemical composition of the heated sediments is an important factor, and propose that the key to understanding the end-Permian terrestrial mass extinction is the vast evaporite deposits in the Tunguska Basin that were heated by large volumes of ascending magma 252 million years ago. There are numerous open questions to be answered regarding the end-Permian extinction in general and the gas venting hypothesis in particular, especially the link between the terrestrial and marine extinctions. However, our results strengthen the ozone depletion mechanism as one of the cause of the terrestrial mass extinction.

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