Siberian gas venting and the end-Permian environmental crisis

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The end of the Permian period is marked by global warming and the biggest known mass extinction on Earth. The crisis is commonly attributed to the formation of the Siberian Traps Large Igneous Province although the causal mechanisms remain disputed. We show that heating of Tunguska Basin sediments by the ascending magma played a key role in triggering the crisis. Our conclusions are based on extensive field work in Siberia in 2004 and 2006. Heating of organic-rich shale and petroleum bearing evaporites around sill intrusions led to greenhouse gas and halocarbon generation in sufficient volumes to cause global warming and atmospheric ozone depletion. Basin scale gas production potential estimates show that metamorphism of organic matter and petroleum could have generated >100,000 Gt CO₂. The gases were released to the end-Permian atmosphere partly through spectacular pipe structures with kilometre-sized craters. Dating of a sill intrusion by the U–Pb method shows that the gas release occurred at 252.0±0.4 million years ago, overlapping in time with the end-Permian global warming and mass extinction. Heating experiments to 275 °C on petroleum-bearing rock salt from Siberia suggests that methyl chloride and methyl bromide were significant components of the erupted gases. The results indicate that global warming and ozone depletion were the two main drivers for the end-Permian environmental crisis. We demonstrate that the composition of the heated sedimentary rocks below the flood basalts is the most important factor in controlling whether a Large Igneous Provinces causes an environmental crisis or not. We propose that a similar mechanism could have been responsible for the Triassic-Jurassic (~200 Ma) global warming and mass extinction, based on the presence of thick sill intrusions in the evaporite deposits of the Amazon Basin in Brazil.

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The Tunguska basin (Fig. 1) is petroleum-bearing, with numerous reservoirs of oil and gas (Fig. 2). Carbonates and minor sandstone and shale horizons dominate the Cryogenian and Tonian (formerly Riphean) source rock sequences which are overlain by the carbonate and evaporate facies of the Ediacaran (formerly Vendian). Furthermore, enormous volumes of Cambrian evaporites are present in the basin, with up to 2.5 km thick sequences of halite-rich strata, anhydrite, and carbonates (Fig. 2) (Zharkov, 1984; Petrychenko et al., 2005). Five major phases of salt deposition occurred in the Cambrian, the most extensive being the 2 million km² Early Cambrian Usoye salt basin with an average of 200 m of halite (Zharkov, 1984). Note that the “Tunguska Basin” in the literature is frequently included in the terms “Siberian Platform” and “Siberian Craton”, and that the Tunguska Basin is often considered as one of many basins situated on the platform/craton. We use the term to encompass all the post Neo-Proterozoic sedimentary rocks on the platform/craton.

The total thickness of the basin stratigraphy commonly varies between 3 km and 12.5 km (Meyerhoff, 1980; Kontorovich et al., 1997), however the Neo-Proterozoic rocks are locally present as 7–10 km thick rift segment deposits (Sokolov et al., 1992; Kuznetsov, 1997; Drobot et al., 2004). Post-Cambrian rocks comprise carbonates, marls, sandstones, and coal (Fig. 2), and the sedimentation terminated in the latest Permian with the onset of Siberian Traps volcanism.

The Tunguska Basin sediments were intruded by the sub-volcanic part of the Siberian Traps. Sills and dykes are abundant throughout the basin, and form sheets up to 350 m thick, locally comprising up to 65% of the stratigraphy (Meyerhoff, 1980; Fedorenko and Czamanske, 1997; Ulmishek, 2001). The maximum accumulated sill thickness in the Cambrian to Permian strata is 1200 m (Kontorovich et al., 1997). The thickness of sill intrusions in the Neo-Proterozoic rocks is uncertain due to a limited number of deep boreholes in the bulk part of the basin (Fig. 2). However, thick sills are commonly present at the base of the Cambrian evaporate sequence (Kontorovich et al., 1997; Ulmishek, 2001). The present day area with outcropping sill intrusions is at least 1.6 million km² (Fig. 1). The sill emplacement led to widespread contact metamorphism of the host sediments (e.g., Kontorovich et al., 1997) and to enhanced maturation of organic matter and the formation of methane-rich petroleum accumulations (Sokolov et al., 1992). The most profound results of the magma-sediment interaction are spectacular magnetite-rich breccia pipes rooted in the Cambrian evaporites or possibly deeper. These pipes are numerous in the southern parts of the basin, where they are filled with up to 700 m deep and 1.6 km wide.

**Fig. 1.** Geological map of the Tunguska Basin in Eastern Siberia, Russia. Note the high abundance of phreatomagmatic pipes with magnetite south of latitude 64°, and the numerous basalt-filled pipes north of 68°. Our main study area during a 2004 field campaign is indicated by the star symbol. The aerial extent of evaporite is from Zharkov (1984). The geological map is modified from Malich et al. (1974), and the positions of the pipes were compiled from various sources (Malich et al., 1974; Nikulin and Von-der-Flaass, 1985; Pukhnarevich, 1986; Von der Flaass and Naumov, 1995; Ryabov et al., 2005; Ryabov, 2006). The outline of the Cambrian evaporite is from Petrychenko et al. (2005), comprising a total area of 2 million km².
About 250 mineralized pipes with magnetite matrix are identified in petroleum reservoirs in the Tunguska Basin (Meyerhoff, 1980). The stratigraphy is characterized by crater lake deposits (Von der Flaass and Naumov, 1995; Von der Flaass, 1997). About 250 mineralized pipes with magnetite matrix are identified in the basin based on aero-magnetic surveys. Several of these are currently mined for magnetite. Many more pipes, especially without magnetite, are likely present due to the poor rock exposures on the Siberian taiga. For instance, pipes without magnetite mineralization are known in the northern parts of the Tunguska Basin (Fig. 1), especially without magnetite mineralization. The Cambrian strata vary considerably (1–10 km) but have only been drilled to Upper Cambrian levels, as at Nepa (see Fig. 3). The inferred source region of the pipes, where intense magma-sediment interactions took place, is likely within the lower Cambrian strata. Craters are filled with up to 750 m of crater-lake sediments (Von der Flaass and Naumov, 1995; Von der Flaass, 1997).

Siberian Traps lava flows are covering parts of the Tunguska Basin (Meyerhoff, 1980). The stratigraphy is considered representative for the basin segment with pipes. The thicknesses of the pre-Cambrian strata vary considerably (1–10 km) but have only been drilled in the central parts of the basin. Sill intrusions are present throughout the basin stratigraphy (Kontorovich et al., 1997). The pipes are rooted in the Cambrian evaporite or possibly deeper, but have only been drilled to Upper Cambrian levels, as at Nepa (see Fig. 3). The inferred source region of the pipes, where intense magma-sediment interactions took place, is likely within the lower Cambrian strata. Craters are filled with up to 750 m of crater-lake sediments (Von der Flaass and Naumov, 1995; Von der Flaass, 1997).

**Fig. 2.** Schematic stratigraphy with compiled information about the occurrences of petroleum reservoirs in the Tunguska Basin (Meyerhoff, 1980). The stratigraphy is considered representative for the basin segment with pipes. The thicknesses of the pre-Cambrian strata vary considerably (1–10 km) but have only been drilled in the central parts of the basin. Sill intrusions are present throughout the basin stratigraphy (Kontorovich et al., 1997). The pipes are rooted in the Cambrian evaporite or possibly deeper, but have only been drilled to Upper Cambrian levels, as at Nepa (see Fig. 3). The inferred source region of the pipes, where intense magma-sediment interactions took place, is likely within the lower Cambrian strata. Craters are filled with up to 750 m of crater-lake sediments (Von der Flaass and Naumov, 1995; Von der Flaass, 1997).

Craters are filled with up to 750 m of crater-lake sediments (Von der Flaass and Naumov, 1995; Von der Flaass, 1997). About 250 mineralized pipes with magnetite matrix are identified in the basin based on aero-magnetic surveys. Several of these are currently mined for magnetite. Many more pipes, especially without magnetite, are likely present due to the poor rock exposures on the Siberian taiga. For instance, pipes without magnetite mineralization have been discovered by coincidence during mining. In addition, more than 500 basaltic diatreme-like pipes are known in the northern parts of the Tunguska Basin (Fig. 1).

Siberian Traps lava flows are covering parts of the Tunguska Basin, and comprise up to 6500 composite meters in the north (e.g., Federenko and Czamanske, 1997; Kamo et al., 2006). Lava flows are not outcropping south of ~60°, and the absence of lava within the crater-lake deposits suggests that lava flows never formed an extensive cover in the southern parts of the basin. However, pyroclastic rocks are abundant in interval of 68 to 62° (e.g., Federenko and Czamanske, 1997; Kamo et al., 2006), but their formation and source remains poorly understood.

The Cambrian evaporite strata in the Nepa area contain sills, contact aureoles, and volcanic breccia pipes of Siberian Traps age (Fig. 3). A 2004 field campaign to Nepa (N 59° and E 107°; Fig. 1) was targeted at cores drilled at Nepa in the 1970’s and 80’s for potassium salt prospecting. The site is unique as the drilled salt is preserved, the cores are largely intact, and it was possible to identify core tray labels during field work. The on-site work included mapping, borehole logging, and sampling of end-Permian pipe structures. A 200 m thick mafic sill is located in the upper Cambrian strata, and a second level of sills was discovered in the section. The upper sill has a maximum thickness of 326 m in the Nepa area (Zamaraev et al., 1985). The sills and pipes are associated with extensive hydrothermal alteration zones and contact aureoles. The northermmost pipe structure at the Nepa locality, the Scholokhovskoe pipe, is characterized by five main breccia lithologies with varying degrees of magmatic and sedimentary fragments (Fig. 4).

**3. Methods**

**3.1. Heating experiments**

Gas extraction and heating experiments were conducted at the Norwegian Institute for Air Research on natural rock salt samples from the 194 borehole at Nepa (Fig. 3). Eight samples were analysed, all containing petroleum-bearing fluid inclusions. Salt from the interior of the cores were selected for analyses to minimize possible contamination during drilling, storage, and sampling. Contamination is accordingly regarded as minimal, also considering that compounds formed from heating of wood fragments or plastic bags would easily be identified during the heating runs. Between 2 and 4 g of sample were gently crushed to 3–10 mm pieces and split in two fractions. Gas was flushed through Perkin Elmer stainless steel adsorption tubes prior to desorption at 250 °C for 7.5 min, followed by GC-MS analyses on a Hewlett Packard 6890A with a detector temperature of 225 °C, and a 1 µm DB-1701 32 m separation column. The analyses are semi-quantitative and measured relative to a toluene standard. The degree of adsorption in the tubes is 10–50% for light gases, thus significantly underestimating the actual concentrations. Furthermore, CO2 and CH4 are not adsorbed in the tubes. However, the analytical setup is efficient in terms of analyzing halocarbons, which are the targeted gas compounds in this study.

The first set of samples was crushed in a 20 ml sealed steel chamber in an argon atmosphere at room temperature, and a known volume of gas was sucked through the adsorption tubes by a pump. The second set of samples was used in heating experiment to investigate the potential for gas synthesis. The crushed samples were placed directly in the adsorption tubes and heated to 275 °C within the thermodesorption oven in a helium atmosphere. The released gases were continuously trapped at −60 °C before transfer to the GC-MS.

**3.2. Gas production potential**

We have applied the following relationship to calculate the gas production potential 

\[ W_p = V_p \times \rho \times S \]

where \( W_p \) is the aureole volume (sill area times aureole thickness), \( V_p \) is the rock density, and \( S \) is the aureole shape parameter defined as the TOC profile through the aureole (Svensen et al., 2007). We assume a linear relationship in carbon loss proportional to the aureole volume. Generally, contact aureoles have the same thicknesses as their respective sills, both below and above intrusions in low permeability sediments.
This implies that the total volume of sediments affected by contact metamorphism is equal to twice the sill volume. Note that the gas will be produced in the aureole independent of the specific type of organic material undergoing metamorphism (dispersed organic matter, coal beds, or petroleum). The mass conversion factors for calculating gas equivalents from carbon are 1.34 and 3.66 for methane and carbon dioxide, respectively.

3.3. Dating

U–Pb analyses on two dolerite samples from the 194 borehole (sampled at 860.8 m and 868.7 m) (Fig. 2) were carried out using ID–TIMS (isotope dilution thermal ionization) and a Finnigan MAT262 instrument at the Department of Geosciences in Oslo. The 20 to 30 zircon grains found in each of the two samples occurred largely as fragments, locally with some preserved euhedral faces. Most grains showed some local turbidity, fractures or inclusions of other minerals. Baddeleyite was only observed as an inclusion in one zircon. Abrasion generally removed most of the turbid parts of the fragments. The best grains were selected for analysis, some were perfectly clear but others still contained some imperfections. Zircon grains were abraded before analysis, then dissolved and transferred directly to the mass spectrometer for measurement, except for one larger fraction processed through anion exchange resin. A mixed \(^{235}\text{U}–^{206}\text{Pb}\–^{205}\text{Pb}\) spike was used for internal normalization of the fractionation of Pb. See Corfu (2004) for analytical procedures. The data were calculated using decay constants from Jaffey et al. (1971). The uncertainties are 2\(\sigma\).

4. Results

4.1. The breccia

The magmatic fragments of the Scholokhovskoie pipe are rich in glass (Fig. 4), demonstrating rapid melt quenching in the pipe, and the pipe formation was accordingly contemporaneous with the sill emplacement. Hydrothermal minerals include calcite, dolomite, halite, garnet, epidote, and chlorite, either as pore filling minerals or alteration products from igneous fragments.

4.2. Gas generation experiments

Heating experiments on evaporite samples from the 194 borehole were done to determine the type of gas generated during contact metamorphism in the Tunguska Basin. We use natural rock samples equivalent to those that were heated by sills during the end-Permain. The samples were collected at depths between 807 and 949 m, including two reference samples from the contact aureole of the lower sill (Table 1). The samples consist of coarse grained halite with minor sylvine, anhydrite, and pyrite. Trails of liquid and gas inclusions are abundant in the salt (Grishina et al., 1998), releasing aromatic and sulphurous gases when crushed. Table 1 show that butane, benzene, and sulphur-bearing gases are the most abundant of the analysed petroleum compounds at room temperature. Sulphur dioxide is identified in most samples, whereas only two samples contain dimethyl sulphide. Note that no halocarbons were detected.
When the samples were heated to 275 °C for 7.5 min in an inert atmosphere the concentrations of sulphur dioxide increased significantly (up to 130 times), and the concentration of other sulphur gases and hydrocarbons decreased (up to 30 times less butane). It is important that halocarbons like methyl chloride and methyl bromide were identified in all heating runs, as these compounds were not present at room temperature. Maximum concentrations of methyl chloride was 161 ng/g rock for sample 194/4. The mass ratio of methyl chloride to methyl bromide is between 6.6 and 58.6 with an average of 17.3 for the 8 experiments. We use the highest value (i.e., 60) to calculate the methyl bromide generation during contact metamorphism, as bromide is present in significantly lesser amounts in the sedimentary rocks compared to chloride. Halogenated butane, especially 1-chloro-butane, is present in considerable amounts (up to 51 ng/g rock) in all runs except one (sample 194/3). When extrapolated, only 1–350 mg of methyl chloride was generated per m³.

Fig. 4. Fieldwork and sampling in eastern Siberia. A) The 3000 m wide Zheleznogorsk pit is located 350 km south-west of Nepa. The pipe is mined for magnetite. This phreatomagmatic pipe is of similar type as the one studied at Nepa. The pipe itself is outlined on the figure (stippled) and cuts the surrounding Ordovician sediments (carbonates and sandstones). It is one of 5–6 magnetite-bearing pipes that are currently mined in the Tunguska Basin. B) Parts of the remaining core storage at Nepa, now exposed to weather. Core logging and sampling was conducted on site in 2004. C) Altered volcanic breccia from the 6C borehole. The matrix minerals include chlorite, epidote, magnetite, and halite. D) Phreatomagmatic breccia with altered sedimentary fragments (red) in a fine grained volcanic matrix (black and grey). Halite is identified as cement in the breccia. E) Dolerite fragment dominated by glass (black) and plagioclase phenocrysts (grey).
4.4. Age of sill emplacement

Ch3Cl/CH3Br 6.6 8.4 58.6 10.3 8.4 9.3 9.4 27.2
1-bromo-butane 0 7.4 0.03 6.7 0 12.6 5.5 0
1-chloro-butane 8.1 7.3 0 19.3 29.8 50.9 24.1 11.1
Methyl bromide 0.9 2.1 0.01 15.6 0.7 1.3 1.0 0.13
Methyl chloride 5.8 17.7 0.5 161 5.9 12.1 9.1 3.5
Benzene 20.6 36.2 7.0 3.7
Butane 8.1 4.4 6.1 13.3 2.0 2.0 0 3.9 2.3 3.0 0.2 4.8 1.7 10.6 3.7 1.5
200 m thickness (e.g., Vasil’ev, 1999) in an area of 2 million km2 with density of 2.3 g/cm3. Note that this approach underestimates the gas assume that between 0.5 and 1.5 wt.% of organic matter reacted to gas, (i.e., one pipe per 312 km2). We can extend this coverage to the poorly contact metamorphism.

4.3. Gas production potential

The gas production potential (Svensen et al., 2004) during meta-

morphism of the Tunguska Basin sediments has been estimated based on basin scale metamorphism of organic carbon. We have used two approaches to estimate the carbon gas production potential during contact metamorphism of the Tunguska basin sediments during sill emplacement and pipe formation. 1) Pipe source region. Assumes a 5 km3 pipe source region, a 2–5 wt.% conversion of organic matter to gas, and a rock density of 2300 kg/m3. 2) Basin scale gas generation in contact aureoles (Svensen et al., 2004). Here we assume the emplacement of one sill of 200 m thickness (e.g., Vasil’ev, 1999) in an area of 2 million km2 with pipes, shale, evaporite, and petroleum (Fig. 1), leading to a sill volume of 400,000 km3 and hence an aureole volume of 800,000 km3. Finally, we assume that between 0.5 and 1.5 wt.% of organic matter reacted to gas, and that this comprised half of the bulk rock TOC in the aureole with a density of 2.3 g/cm3. Note that this approach underestimates the gas production because there are multiple sill emplacement levels in the basin (cf. Kontorovich et al., 1997), and the metamorphism may locally have affected layers with higher TOC contents higher than 3 wt.% (cf. Kuznetsov, 1997). Furthermore, CO2 generation from metamorphism of dolostone is not included in the estimates, but represents a potentially significant source of isotopically heavy carbon (δ13C ~ −4 to +2% VPDB). We assume a CH3Cl/TOC of 0.49 (Beerling et al., 2007), and a CH3Cl/CH3Br of 60 (this study).

The resulting basin scale carbon gas production potential is between 9200 and 27,600 Gt C (Table 2). The results from the calculations based on the pipes show that the production potential per pipe is 0.23–0.58 Gt C. Mapping of pipes has been most extensive in the Bratsk region where about 200 pipes are known in a 250 × 250 km (62,500 km2) large area (i.e., one pipe per 312 km2). We can extend this coverage to the poorly exposed 2,000,000 km2 large basin with evaporites, resulting in a total of 6400 pipes in the basin. The results in a potential for generating 1500–3700 Gt C in the pipe source regions (Table 2).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>194/5</th>
<th>194/2</th>
<th>194/3</th>
<th>194/4</th>
<th>194/9x</th>
<th>194/21x</th>
<th>194/30</th>
<th>194/32</th>
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<td>Depth</td>
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<td>807.2</td>
<td>819.4</td>
<td>824.4</td>
<td>880.1</td>
<td>937.9</td>
<td>949.3</td>
<td>194/5</td>
</tr>
<tr>
<td>Method</td>
<td>Room temperature, ng gas/g rock</td>
<td>Heating and extraction at 275 °C, ng gas/g rock</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sulfur dioxide</td>
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<td>0.03</td>
<td>0.3</td>
<td>1.3</td>
<td>0</td>
<td>1.1</td>
<td>0.2</td>
<td>1.4</td>
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<tr>
<td>Methyl tioetane</td>
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<td>35.7</td>
<td>114.2</td>
<td>11.5</td>
<td>7.4</td>
<td>0.03</td>
<td>6.7</td>
<td>0</td>
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<tr>
<td>Benzen</td>
<td>0.9</td>
<td>2.1</td>
<td>0.01</td>
<td>15.6</td>
<td>0.7</td>
<td>1.3</td>
<td>1.0</td>
<td>0.13</td>
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<tr>
<td>Methyl chloride</td>
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<td>17.7</td>
<td>0.5</td>
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<td>5.9</td>
<td>12.1</td>
<td>9.1</td>
<td>3.5</td>
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<tr>
<td>Benzene</td>
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<td>36.2</td>
<td>7.0</td>
<td>3.7</td>
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<td></td>
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<td>Butane</td>
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<td>4.4</td>
<td>6.1</td>
<td>13.3</td>
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<td>0</td>
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<tr>
<td>Ch3Cl/CH3Br</td>
<td>8.4</td>
<td>9.3</td>
<td>9.4</td>
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<td>7.0</td>
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<td></td>
</tr>
</tbody>
</table>

*Sample affected by contact metamorphism.

shows that the effect is insignificant. The analyzed zircon grains are very rich in U (~700 ppm–21,800 ppm) and also have high Th/U ratios (1.5–3.5). The spread in ages is therefore most likely a result of partial Pb loss. The uppermost analyses, however, appear to have escaped disturbances because the weighted average of their 206Pb/238U age of 252.0 ± 0.4 Ma. This is corroborated by the upper intercept age of 252 ± 1.2 Ma of the regression line through all 11 data points. The age of 252 ± 0.4 Ma is thus considered the best estimate for crystallization of the sill intrusion.

5. Discussion

5.1. Volatile generation

The source rocks of the Tunguska Basin reached peak maturity during the Carboniferous (Meyerhoff, 1980; Ulmishek, 2001), but petroleum generation started as early as in the Neo-Proterozoic (Sokolov et al., 1992). This means that the basin was petroleum-bearing prior to the end-Permian sill emplacement. The TOC values in rocks affected by contact metamorphism, which form the basis for estimating the carbon gas production potential, are uncertain due to few boreholes penetrating the source rocks in the deep central parts of the basin. However, assuming that the available data from the basin margins are representative, a 1–3 wt.% TOC is supported (Sokolov et al., 1992; Kuznetsov, 1997; Bartley et al., 1998; Ulmishek, 2001). Organic carbon values as high as 8–22 wt.% are present locally in source rocks (Sokolov et al., 1992; Kuznetsov, 1997; Drobot et al., 2004). In addition, sills have intruded petroleum-bearing Ediacaran and Cambrian levels, where 8–10 vol.% petroleum fill is present in carbonate reservoirs (e.g., Meyerhoff, 1980; Kuznetsov, 1997). The metamorphism also led to enhanced petroleum migration (e.g., Polyanskiy and Reverdatto, 2002).

From the composition of the sediments undergoing contact meta-
morphism, gases like CH4 and CO2 (from carbonates, organic matter, and petroleum), SO2 (from evaporites) were released, in addition to
minor volumes of magmatic volatiles (CO₂, HCl, SO₂). This is supported by gas geochemistry from the Tunguska Basin, and methane-generation during contact metamorphism is considered the final phase of petroleum formation in the basin (Sokolov et al., 1992). Moreover, high concentrations of organic sulphur-compounds (mercaptans) have been identified in oil and condensates, attributed to the contact metamorphism (Kontorovich et al., 1997). Note that the same compounds were identified during initial gas extraction from the contact aureole salt samples (Table 1).

The basin scale gas production potential estimates shows that contact aureoles in the Southern Tunguska Basin could have generated between 9200 and 27,600 Gt C (equivalent to 33,700–101,000 Gt CO₂). In addition, the pipes released 1500–3700 Gt C (equivalent to 5400–13,500 Gt CO₂). This estimated number of pipes is high (6400), but is still considered realistic as it is within the same order of magnitude as the number of hydrothermal vent complexes in the Karoo Basin in South Africa (Svensen et al., 2006, 2007) and in the Voring Basin offshore Norway (Svensen et al., 2004; Planke et al., 2005). In the Voring Basin, there are about 2500 hydrothermal vent complexes in an 85,000 km² large basin segment (i.e., one pipe per 34 km²). Assuming that each pipe in the Tunguska Basin has a source region of 5 km², the resulting volume of high temperature sediment metamorphism for the 6400 pipes is 32,000 km³. This leads to an aureole-volume to pipe-volume ratio of 25. The pipes likely formed in regions with a higher gas production potential at the base of the Cambrian evaporite sequence, thus we use a conversion of 2–5 wt.% organic matter to gas.

5.2. Gas experiment

The heating-experiments, although being semi-quantitative, suggest that a series of sulphur gases and halocarbons were generated during metamorphism in addition to the carbon gases. To our knowledge, this is the first experimental demonstration that natural rock samples generate halocarbons during heating. We attribute the halocarbon generation to reactions between the petroleum bearing fluid inclusions and the host salt on the prograde temperature path to 275 °C. A requirement for methyl chloride generation from organic matter is the presence of chloride ions and methyl groups (Conesa et al., 1997; Kepper et al., 2000; Hamilton et al., 2003). In the salt samples, the chloride is present in the inclusion fluid water, and methyl groups are produced from the petroleum during heating. An equivalent process is likely responsible for the formation of 1-chloro-butane, methyl bromide and 1-bromo-butane. Assuming that the gas speciation is not too pressure sensitive, the experiments show that halocarbons are natural products of contact metamorphism of the Tunguska Basin evaporites.

5.3. Pipe processes

The pipes in the Tunguska Basin were formed as a consequence of the pressure build-up during heating of the Precambrian and Cambrian sequences (Von der Flaass and Naumov, 1995; Von der Flaass, 1997). Pressure build-up mechanisms contributing to pipe formation include heating of pore fluids and metamorphic devolatilization of carbonate, shale, liquid hydrocarbon and brine reservoirs, and halite-anhydrite rocks, generating gases like CH₄, CO₂, and SO₂ (cf. Jamtveit et al., 2004; Svensen et al., 2007). Cracking of liquid petroleum to gas could have been of major importance for pipe formation, as cracking at atmospheric conditions results in a 700 fold volume increase (Barker, 1990). Even at higher pressures, this conversion would lead to accelerated hydrofracturing and vertical fluid expulsion. In the Tunguska Basin, reactions with the evaporites likely generated sulphurous gases and halocarbons, as shown

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Weight³</th>
<th>U⁰</th>
<th>Th/U</th>
<th>Pb²²⁰/²³⁵</th>
<th>Pb²⁰⁶/²³⁵</th>
<th>Pb²⁰⁷/²³⁵</th>
<th>Rho²⁰⁷/²³⁵</th>
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<td>[pg]</td>
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<td>[abs]</td>
<td>[abs]</td>
<td>[abs]</td>
<td>[age in Ma]</td>
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<tr>
<td>194/15–868.7 m, mafic sill</td>
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<td></td>
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<tr>
<td>Z fr [1]</td>
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<td>&gt;920</td>
<td>1.9</td>
<td>1.6</td>
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<td>0.03984</td>
<td>0.00014</td>
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1 Z=zircon; fr=broken pieces of crystals, locally with euhedral faces (=eu); im=slight imperfections (local turbidity, rust or inclusions) |N|=number of grains in fraction.
2 Weight and concentrations are known to better than 10%, except for those near the ca. 1 g limit of resolution of the balance.
3 Th/U model ratio estimated from 208/206 ratio and age of sample.
4 Pb=total common Pb in sample (initial+blank).
5 Raw data corrected for fractionation.
6 Corrected for fractionation, spike, blank and initial common Pb; error calculated by propagating the main source of uncertainty.
by our experiments. Gas generation from sediment metamorphism is known both from the Karoo Basin in South Africa and offshore Norway, resulting in vertical piercement structures (Jamtveit et al., 2004; Svensen et al., 2004; Svensen et al., 2007). The main differences in the pipe forming mechanisms between these two settings and the one in Siberia, is the presence of evaporites and petroleum in the source region, and extensive magma-sediment interactions within the pipes. The pipes are rooted at 2–4 km depth in magma-sediment mixing zones, probably close to the base of the evaporite stratigraphy although the precise nature of the roots remains unknown. Fig. 6 shows the schematic evolution of the pipe structures. The sizes of the pipe craters in the Tunguska Basin suggest powerful eruptions, with gases and ash likely reaching high atmospheric levels. The presence of glass in the Scholokhovskoe breccia pipe suggests that the pipe was formed as a phreatomagmatic event, where the partly molten magma cooled rapidly in the pipe during eruption. Parts of the wall-rock collapsed into the pipe, mixing with the

![Fig. 6. Schematic evolution of the Tunguska Basin pipes and the venting of carbon gases and halocarbons to the atmosphere. The pipe evolution is partly based Von der Flaass and Naumov (1995) and Von der Flaass (1997). 1) Emplacement of sills into organic rich sediments and evaporites with petroleum accumulations (P). 2) Contact metamorphism of shale, evaporite, and petroleum, leading to gas generation and overpressure (shown as stippled lines). Melt is accumulating within evaporite sequences in the source region of the pipe. 3) Pipe formation and eruption. Glass in the breccias show that the magma was disrupted and fragmented in the source region before vertical transport and phreatomagmatism. Powerful eruptions led to wide craters and subsidence. Gases generated in contact aureoles are now released to the atmosphere. 4) Continued degassing from both magma and sediments through the pipe and the crater-lake. Contact metamorphism of shallow organic-rich sequences (coal) along dikes, and appearance of the first lava flows further to the north in the basin. The inferred gas composition is shown in the frame, alongside the estimated carbon gas and halocarbon production potential for the pipe degassing alone.](image)

![Fig. 7. Compilation of zircon U–Pb ages of key end-Permian events. The ages of the P–T boundary are from (Gradstein et al., 2004) deduced from Bowring et al. (1998) (stippled, labelled “B”), and from a revised age by Mundil et al. (2001) (in grey, labelled “M”). The age of the sill emplacement at Nepa (this study) is synchronous with pipe formation and release of carbon gases and halocarbons to the atmosphere. The main phase of the extinction is dated to have occurred between 252.3±0.3 and 251.4±0.3 Ma by Bowring et al. (1998) (labelled “B”) and 252.6±0.2 Ma by Mundil et al. (2004) (labelled “M”).](image)
breciated sediments from the root zone and the magmatic material. Degassing of metamorphic volatiles continued along with circulation of brines and metamorphic reactions between fluids and breccia, as suggested by the hydrothermal mineralogy. The world-class magnetite reserves of the Tunguska Basin pipes likely originated from hydrothermal leaching of iron by hypersaline brines from the source region followed by precipitation in the breccia (e.g., Mazurov et al., 2007).

5.4. Timing, timescales, and fluxes

The sill dating demonstrates that sill emplacement at Nepa occurred 252.0±0.4 Ma, overlapping the U–Pb age of 252.6±0.2 Ma for the main phase of the end-Permainian extinction (Fig. 7) (Mundil et al., 2004). This supports a causal link between the pipe degassing and the end-Permainian environmental crisis.

If the contact metamorphic gas wholly or partially vented to the atmosphere, the result would be global warming even for a 100 ky degassing scenario (c.f., Berner, 2002; Retallack and Jahn, 2008). The released gas would have a δ13C isotopic composition close to that of bulk oil and organic matter (−30 to −25‰) (Hunt, 1979). The widely used δ13C composition of volcanic CO2 is about −6‰, and would in that case be too isotopically heavy to have caused the end-Permainian negative carbon isotope excursion (c.f., Berner, 2002). The isotopic composition of the released CO2 from the Siberian Traps flood basalts is not known, but is assumed to be close to −6‰. Sill emplacement and pipe formation is considered a rapid process (Jamtveit et al., 2004; Svensen et al., 2004), and we assume that one pipe formed per year in the Tunguska Basin. We stress that this is a hypothetical assumption in order to evaluate the carbon gas fluxes. The assumption is nevertheless realistic, as only a limited volume of melt is required to form even the most widespread sill intrusions, and contact metamorphism and venting occurs on timescales of 10–100 years (Jamtveit et al., 2004). Still, we cannot exclude that the pipe eruptions could have been clustered in time or formed during a period of a few tens of thousands of years. The chosen model scenario implies a total duration for the pipe degassing of 6400 years, and an integrated CO2 equivalent flux of 0.8–2.1 Gt CO2/y. Seepage from contact aureoles started after the pipe degassing, releasing 0.7–2.0 Gt CO2/y over a 50 ky period. Note that this is less than the 2000–2005 average anthropogenic emissions of about 25–28 Gt CO2/y (IPCC, 2007).

The CO2 flux from the lavas is based upon the Siberian Traps lava volume estimate by Reichow et al. (2002), a 1 million year emplacement period, and the CO2 basaltic lava degassing estimate by McCartney et al. (1990) and Self et al. (2005) (giving 0.024 and 0.017 Gt C/y, respectively). Note that a few thick lava flows or sill intrusions would have led to perturbations in the carbon degassing, with major consequences for the atmospheric composition.

5.5. Implications for the end-Permainian ozone layer

Generation and venting of chlorinated and brominated halocarbons, both of which are synthesized in the evaporites, could have environmental consequences due to the involvement of halocarbons in stratospheric ozone depletion (Beerling et al., 2007). Based on mass balance calculations, between 4500 and 13,500 Gt methyl chloride could have been produced during the basin-scale metamorphism (Table 2), and additional 720–1800 Gt during pipe degassing. The fluxes of methyl chloride according to the model scenario are 0.11–0.28 Gt/y for the pipe stage and 0.09–0.27 Gt/y for the seep stage. Recent atmospheric modeling 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/y (Beerling et al., 2007). Methyl bromide will escalate this process, and our results show that 2–5 Tg methyl bromide could have been released during the pipe degassing stage per year. Even if the halocarbon degassing plume was restricted to lower atmospheric levels, coeval emissions of methane would enable the halocarbons to pass the troposphere without reacting with OH (see Beerling et al., 2007).

To conclude, the metamorphism and venting in the Tunguska Basin can successfully be applied as a mechanism to explain several of the end-Permainian extinction hypotheses: a) extinction from global warming and hypercapnia (e.g., Knoll et al., 2007), b) extinction from ozone layer collapse and high levels of surface radiation (e.g., Visscher et al., 2004; Foster and Afonin, 2005; Kump et al., 2005; Beerling et al., 2007; Lammert et al., 2007).

6. Conclusions

We conclude that the pipe structures in the Tunguska Basin provide direct evidence for end-Permainian carbon gas and halocarbon release to the atmosphere synchronous with sill emplacement. The end-Permainian crisis can be attributed to element mobilization from the evaporites (producing halocarbons) and organic-rich deposits (producing greenhouse gases like CH4 and CO2) in Siberia. For the first time, we show that halocarbons are generated when natural evaporite samples are heated to 275 °C, simulating the conditions during contact metamorphism. Basin scale gas production potential during metamorphism shows that carbon gases were generated in sufficient quantities to explain the end-Permainian negative carbon isotope excursion and global warming. Moreover, our results explain how the Siberian Traps intrusions led to a mass extinction whereas the formation of many other Large Igneous Provinces did not: two kilometres of intruded evaporite made the difference.

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