## = GEOCHEMISTRY =

## Juvenile Flow of Carbon Dioxide and Causes of Global Environmental Changes at the Permian–Triassic Boundary

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Among the causes of catastrophic global climatic changes accompanied by mass extinction of flora and fauna, the main one is giant impact events and intensification of magmatic activity related to the ascent of mantle superplumes over certain geologic time intervals. The most prominent crisis in the history of the biosphere occurred at the Permian–Triassic boundary. The majority of researchers refer it to the enormous lava eruptions in the Siberian trap province (STP) at the above stratigraphic boundary [1], although it has also been suggested that this biocrisis was provoked by a cosmic catastrophe [2, 3].

Much importance is also attached to the emission of volcanic carbon dioxide and acid gases (SO<sub>2</sub>, HCl, and HF) into the atmosphere and hydrosphere as a factor that changes the environment of living organisms. All these components, except CO<sub>2</sub>, affect the environment over short time intervals of several years. The removal of carbon dioxide from the atmosphere is much slower, and its effect as a greenhouse gas may continue for tens of thousand years [3]. Therefore, increase in atmospheric CO<sub>2</sub> concentration may be regarded as the most plausible factor of global changes. This communication presents estimates of the magmatogenic CO<sub>2</sub> influx into the atmosphere at the Permian–Triassic boundary during STP formation.

As in other giant igneous provinces, tholeiitic basalts are most abundant in the STP. This province also includes subordinate amounts of high-Mg volcanics and dike rocks (picrites of the Noril'sk district, meimechites and alkali picrites of the Maimecha–Kotui region, and subalkali picrobasalts of the Putorana Plateau). The role of volatile components is especially evident in these high-Mg rocks. Olivine phenocrysts from subalkali picrites of the Putorana Plateau often contain fluid and composite (melt–fluid) microinclusions filled with dense carbon dioxide (represented by liquid and gas bubbles at room temperature [4]). The occurrence of such composite microinclusions indicates that olivine crystallized under a high pressure along with distillation of gaseous carbon dioxide phase; i.e., the melt was saturated with  $CO_2$  at the earliest stage of the igneous process.

The olivine crystallization depth of the magma chamber can be estimated from geochemistry of the Putorana subalkali picrobasalts. These rocks lack indications of crustal contamination, such as negative Nb–Ta anomaly [5] (the Nb/U ratio is nearly chondritic [6]). At the same time, the Nb–Ta anomaly is clearly expressed in tholeiitic plateau basalts [5]. This implies that the parental magma chambers of plateau basalts were localized within the continental crust, whereas subalkali picrobasalts were derived from a source localized below the Moho surface. In this case, olivine phenocrysts crystallized at a pressure of ~1 GPa.

At 1 GPa, the solubility of  $CO_2$  in the tholeiitic basaltic melt is close to 1 wt %. Subalkali picrobasalt contains much more Ca, Mg, and Fe, and this provides a higher solubility of carbon dioxide [7]. Using the equation that describes the relationship between  $CO_2$ solubility and melt composition [7], one can assess the  $CO_2$  content in a picrobasaltic melt equilibrated with carbon dioxide fluid as ~3 wt %. The high  $CO_2$  content in high-Mg magmas promoted their degassing at great depths and transport of the high-dense melt to the surface [8].

If the CO<sub>2</sub> content in magma is known, we can judge the concentration of this component in a mantle source. In the absence of residual carbonates, highly incompatible elements, such as Nb, Th, or Ba, are geochemical analogues of CO<sub>2</sub>. This follows, for example, from the data on quenched glasses and melt microinclusions in the Siqueiros Fracture Zone [9]. The Nb content in melt inclusions from olivine phenocrysts of subalkali picrobasalt is 45 ppm. Thus, the CO<sub>2</sub>/Nb ratio in this magma is estimated as 660, which is rather close to the value in the primitive mantle (CO<sub>2</sub>/Nb = 670) and the

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primary kimberlite magma. Indeed, phase equilibria in the carbonate-silicate systems show that the CO<sub>2</sub> content in the primary kimberlite magma is estimated as 13–18% [10]. Taking this value into consideration and assuming an average Nb content of 1214 ppm in kimberlites of Group I, we obtain  $CO_2/Nb = 600-840$ . Accepting  $CO_2/Nb = 660$  for the mantle source of Siberian plume and assuming the average Nb content in tholeiitic basalts of the Putorana Plateau to be ~4 ppm. we obtain the CO<sub>2</sub> concentration therein as  $\sim 0.\overline{26\%}$ . Many authors suggest that the total volume of lava that erupted in the STP attains  $2 \cdot 10^6$  km<sup>3</sup>. In this case, the amount of CO<sub>2</sub> emitted into the atmosphere is  $1.5 \cdot 10^{13}$  t. This value is comparable with the CO<sub>2</sub> mass ( $\sim 2 \cdot 10^{13}$  t) required to provide substantial global warming (a mean temperature rise of  $1-2^{\circ}C$  [11].

The aforementioned estimate of the juvenile carbon dioxide mass emitted into the atmosphere at the Permian-Triassic boundary is a minimum, because it does not take into account the amount of carbon dioxide released during the following processes: (a) the emplacement of hypabyssal intrusions (sills) that occupy much larger areas than basaltic flows at the surface; (b) the emplacement of carbonatite magmas into the upper crust within the Maimecha-Kotui province; and (c) the contact metamorphism of sedimentary carbonate rocks of the Siberian Platform. Furthermore, it should be kept in mind that the area of plume magmatism at the Permian–Triassic boundary was actually much larger than had been deemed so far, because recent data indicate that the plume magmatism extends in the buried rifts of western Siberia and the shelf of the Arctic Ocean [12]. Some researchers also assume the contribution of degassing of magmas of the second phase of continental basaltic volcanism in the Emei Shan province (southern China) [13, 14] that were coeval with the Siberian plateau basalt.

In general, it cannot be ruled out that the real quantity of CO<sub>2</sub> emitted into the atmosphere at the Permian– Triassic boundary could be several times more than the minimum estimate of  $1.5 \cdot 10^{13}$  t. Release of such a huge mass of carbon dioxide over a geologically short time (~1 Ma or less) could have undoubtedly provoked the catastrophic global climatic changes and large-scale biocrises of that time.

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Evaporites are widespread in the Paleozoic sedimentary cover of the Siberian Platform. The interaction of basaltic magmas with evaporites might lead to a substantial increase of chlorine and sulfur contents in melts [15]. As a result, not only  $CO_2$ , but also significant masses of HCl and  $SO_2$ , which exert appreciable influence on the environment, could have been emitted into the atmosphere in the course of STP evolution.

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