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## Contact metamorphism of black shales: global carbon cycle and climate perturbations

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There is an increasing interest in improving the understanding of past climate changes, as it can lead to a better understanding of future challenges related to global warming and anthropogenic release of greenhouse gases. The formation of Large Igneous Provinces (LIPs) and sill intrusions in volcanic basins correlate with global warming events and mass extinctions, e.g. the Karoo Basin, South Africa ( $\sim$ 183 Ma), the Møre and Vøring Basins offshore Norway ( $\sim$ 55 Ma), and the Tunguska Basin, Siberia ( $\sim$ 252 Ma). The proxy records from these events suggest that rapid release of large amounts of isotopically <sup>13</sup>C-depleted greenhouse gases (CO<sub>2</sub> and methane) to the atmosphere.

Organic matter stored in sedimentary rocks (e.g. black shale) represents a major carbon source. Large volumes of greenhouse gases may form by contact metamorphism of organic-rich sediments around sill intrusions associated with LIPs. The organic-rich Ecca Group forms the base of the Karoo sedimentary succession and contains thousands of degassing pipe structures rooted in contact aureoles around sill intrusions. Numerical and analogue modelling show that these piercement structures form during violent eruptions releasing the overpressure driven by dehydration and devolatilization metamorphic reactions.

In this study we evaluate the aureole processes numerically in order to constrain the amount of gases formed in contact aureoles around sill intrusions, and the isotopic composition of those gases. The total organic carbon (TOC) in the shale and the intrusion thickness are the most important parameters controlling the amount of carbon gas that can trigger pipe formation and release into the atmosphere.

We model thermal cracking using a general kinetic approach, while dehydration reactions are modeled under the assumption of thermodynamic equilibrium. The theoretical approach is tested against borehole data from the Karoo Basin in South Africa (geochemical analyses, Rock-Eval pyrolysis, TOC, vitrinite reflectance and stable isotopes).

Decreasing TOC content and increasing vitrinite reflectance with decreasing distance to the intrusive contact are signatures of thermogenic hydrocarbon formation. During high temperature metamorphism, formation of carbon gases is preferred over liquid hydrocarbons. However, only limited isotopic fractionation is occurring in the released carbon gases during increasing temperature.

Increasing veining towards the contact of a 10 meter sill suggests that hydrocarbon formation in organic-rich aureoles leads to pressure buildup and fracturing of the aureole, even with small volumes. Our numerical model also shows that sill thicknesses in the order of 100 m are necessary to produce the pressure buildup in the contact aureole and subsequent venting. In addition, mineral dehydration and thermal stresses contribute to pore fluid pressure increase.

We use our numerical model to predict the amount of fluids produced as response to thin ( $\sim$ 10 meter) and thick ( $\sim$ 100 meter) sills. The model provides us with important estimates of rate and duration of gas formation. The time-scale of subsurface gas formation is well within the time scale indicated by the proxy data. Results from isotope compositions demonstrate that the  $2.8t/m^2$  of organic carbon escapes the contact aureole during devolatilization processes involving the generation of light carbon gases. The calculated isotopic composition of the carbon released is similar whether using the batch devolatilization or the Rayleigh distillation model, and ranges from the background values to 1-2 permil lighter values with decreasing distance from the contact.

The extrapolation of our results to the portion of the sedimentary basin intruded by magma suggests that contact metamorphism of organic-rich sediments triggered a potential release of between 2000 to 10000 Gt of isotopically light carbon gas to the atmosphere. In conclusion, the amount and composition of methane that can be produced and vented from contact aureoles in the Karoo Basin during the Toarcian is within the same order of magnitude as required to explain global carbon isotope excursion and hence global warming.