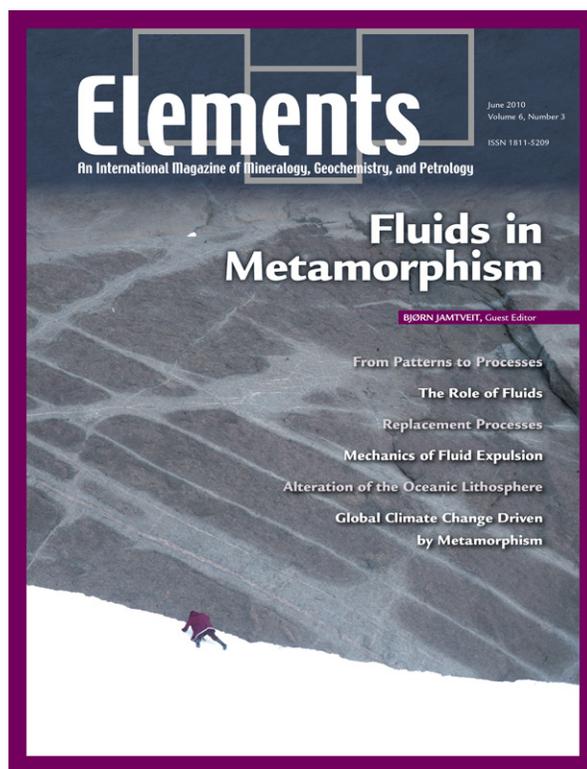


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Metamorphic Fluids and Global Environmental Changes



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Carbon dioxide is produced by metamorphic reactions in orogenic belts and high-heat-flow systems. Part of this carbon is ultimately released to the atmosphere, but the long timescale of regional metamorphism implies that the short-term effects on the environment are minor. However, contact metamorphism around igneous sill intrusions in organic-rich sedimentary basins has the potential to generate huge volumes of CH₄ and CO₂, and these gases are rapidly released to the atmosphere through vertical pipe structures. The high flux and volume of greenhouse gases produced in this way suggest that contact metamorphic processes could have a first-order influence on global warming and mass extinctions.

KEYWORDS: metamorphic carbon degassing, contact metamorphism, large igneous provinces, volcanic basins, rapid environmental changes

INTRODUCTION

Carbon-bearing fluids are constantly seeping from the lithosphere to the Earth's surface and into the atmosphere (e.g. Kerrick 2001; Morner and Etiope 2002). In some places, such as young mountain ranges and high-heat-flow zones, the seepage is more intense than in others. In these settings, fluid expulsion at the Earth's surface is a reflection of metamorphism taking place many kilometers below the surface. Hot springs and mud pots are familiar surface manifestations of metamorphic fluid production. The processes behind the production of C-rich volatiles include reactions that transform carbonates, feldspar, and quartz into amphibole, epidote, pyroxene, garnet, and CO₂ (e.g. Kerrick et al. 1991). Key questions include: How much CO₂ can be generated and released by metamorphic processes? And how fast? Can the degassing trigger rapid global warming and make an impact on life on Earth?

Pioneering work by Derrill M. Kerrick and coworkers in the 1990s attempted to link Cenozoic greenhouse events (see Zachos et al. 2001) to large-scale CO₂ degassing caused by prograde metamorphism of carbonate-bearing rocks (Kerrick et al. 1995; Nesbitt et al. 1995). It was proposed that contact metamorphism of limestone around plutons in western North America in the Eocene released large amounts of metamorphic CO₂ (0.167 gigatons [Gt] per square kilometer per million years) and that this degassing could have contributed to Eocene greenhouse conditions if more than 10⁶ km² were metamorphosed (Nesbitt et al. 1995; Kerrick and Caldeira 1998). Such abundant CO₂ degassing would have exceeded CO₂ consumption by silicate weathering (Kerrick and Caldeira 1993). An Early Cenozoic climatic effect of CO₂ degassing by Himalayan regional metamorphism was however discarded (Kerrick

and Caldeira 1999), but new data suggest that present-day regional metamorphism is a net supplier of CO₂ to the atmosphere (Becker et al. 2008; Evans et al. 2008).

The relatively short duration of Cenozoic greenhouse gas-driven events, which lasted less than 200,000 years, relative to the long duration of orogenesis is a major challenge for the hypothesis that metamorphic CO₂ has affected climate. Several rapid global warming events and mass extinctions are known from the geological record, including the Paleocene-Eocene thermal

maximum (PETM; 55 million years [Ma]), the Toarcian (183 Ma), the end-Permian (252 Ma), and the Triassic-Jurassic (200 Ma) (e.g. Wignall 2001; Courtillot and Renne 2003). The triggering mechanisms of these events are poorly understood. Gas hydrate dissociation, sluggish ocean circulation and anoxia, CO₂ degassing of lava, and CH₄ degassing during metamorphism are among the hypotheses that have been proposed (e.g. Wignall 2001; Cohen et al. 2007; Knoll et al. 2007). However, the temporal correlations among these environmental events, the formation of large igneous provinces (LIPs), and contact metamorphism in sedimentary basins intruded by LIP magmas (TABLE 1) suggest a causal relationship.

VOLCANIC BASINS AND LIPS

Contact metamorphism in sedimentary basins occurs when hot and partly molten igneous intrusions heat the country rocks. These sedimentary basins are called *volcanic basins*. The igneous intrusions are often basaltic and emplaced during LIP formation. Volcanic basins are common along volcanic rifted margins and on cratons (FIG. 1). The intrusions commonly form sheet-like sills and dikes. Sills are commonly sandwiched between sedimentary sequences and can be more than 350 m thick. Because sedimentary basins are among the main crustal reservoirs of organic and inorganic carbon (e.g. IPCC 2001), they have a huge potential for CH₄ and CO₂ generation. A link between contact metamorphism and the PETM was proposed in 2004, based on detailed seismic imaging and borehole studies in the Vøring and Møre basins, offshore Norway (Svensen et al. 2004). This hypothesis provided a new framework for investigating the environmental consequences of metamorphism. The cornerstone of the theory is that gas is rapidly generated from heated organic material in metamorphic aureoles and is subsequently released to the atmosphere as greenhouse gas. Recent results have provided strong evidence that a similar explanation applies

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TABLE 1 MAJOR VOLCANIC BASINS, LARGE IGNEOUS PROVINCES (LIPS), AND ENVIRONMENTAL CHANGES

Volcanic basin	LIP	Sill age (Ma)	Event	Pipe structures	CIE	Mass extinction
Vøring and Møre (Norway)	Northeast Atlantic	55.6	PETM	yes	yes	minor
Karoo (South Africa)	Karoo-Ferrar	182.6	Toarcian	yes	yes	minor
Amazonas (Brazil)	CAMP	~200	Triassic-Jurassic boundary	?	yes	major
Solimoes (Brazil)	CAMP	~200	Triassic-Jurassic boundary	?	yes	major
Tunguska (Russia)	Siberian Traps	~252	Permian-Triassic boundary	yes	yes	major
Sichuan (China)	Emeishan Traps	~261	End-Guadalupian	?	yes	major

Abbreviations: PETM = Paleocene-Eocene thermal maximum; CAMP = Central Atlantic Magmatic Province; CIE = carbon isotope excursion

to other climate events, including the Toarcian (Lower Jurassic), the Triassic-Jurassic, the end-Permian, and the end-Guadalupian (e.g. McElwain et al. 2005; Beerling et al. 2007; Svensen et al. 2007, 2009; Retallack and Jahren 2008; Ganino and Arndt 2009). This hypothesis is supported by geological constraints (e.g. *observed* contact aureoles, sill intrusions, and vertical pipe structures) as well as the fact that metamorphism of organic carbon leads to generation of ¹²C-enriched CH₄, which better explains the available geochemical data than the emission of ¹²C-depleted mantle CO₂ as a result of the degassing of LIP lava.

CONTACT METAMORPHISM AND CARBON DEGASSING

Vast volumes of sedimentary rocks are heated in volcanic basins following sill emplacement (FIG. 1; TABLE 2). Sill intrusions can extend laterally over several hundred kilometers, with thicknesses commonly in the 50–200-meter range, and they can dominate the geology of sedimentary basins (FIG. 2A). A single sill could fill a volume of 5,000 to 20,000 km³. Considering that the thickness of the metamorphic aureole on each side of the sill is commonly about the same as the sill thickness, the volume of heated sediments could be as much as 40,000 km³. Because the contact aureoles reach peak metamorphic conditions (typically 400–500°C) shortly after sill emplacement (tens to

hundreds of years), the metamorphic reactions and associated fluid production are also very fast. If only 1 wt% of the organic carbon in shale or siltstone is transformed into gaseous carbon compounds, the gas production potential associated with a 5,000–20,000 km³ sill is 230–920 Gt C (corresponding to a greenhouse gas equivalent of 310–1200 Gt methane, CH₄). This means that a single melt batch injected into an organic-rich sedimentary basin can generate sufficient methane to cause global warming (Svensen et al. 2004, 2007).

In volcanic basins, there is abundant evidence for rapid injection of the aureole-generated gases into the atmosphere. When sedimentary rocks are heated by magma, decomposition of organic matter, mineral dehydration (generating H₂O and CO₂), and pore fluid expansion or boiling occur on a timescale of years. The resulting overpressure can lead to hydrofracturing and the formation of breccia pipes and hydrothermal vent complexes (e.g. Jamtveit et al. 2004). In the Karoo Basin, South Africa, hydrothermal vent complexes commonly formed in the uppermost 400–500 meters of the basin (FIG. 2). In addition, numerous breccia pipes are rooted in contact aureoles in black shale at deeper levels in the basin (Svensen et al. 2007). Baked grey shales that have lost their organic carbon remain in the pipes (FIG. 3). Vent structures and breccia pipes are characteristic features of many volcanic basins, including the Vøring and Møre basins, the Faroe-Shetland

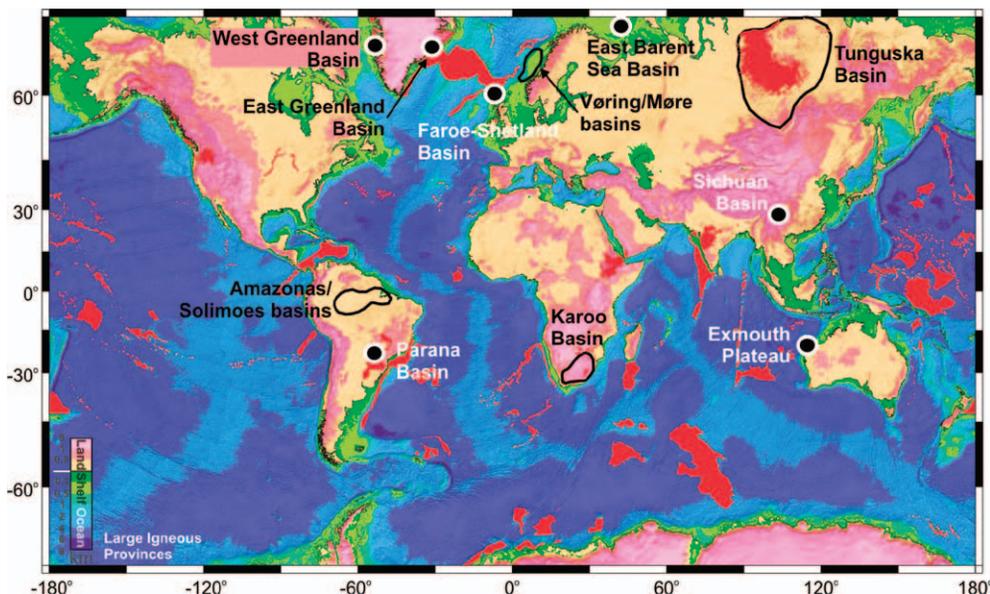


FIGURE 1 Distribution of large igneous provinces (LIPs; basalt lava flows in red) and volcanic basins. Sedimentary basins injected by sills and dikes (i.e. volcanic basins) mentioned

in the text are outlined with heavy lines. Other major volcanic basins are indicated by black filled circles.

TABLE 2 KEY FACTS ABOUT VOLCANIC BASINS

Volcanic basin	Area with sills (x 1000 km ²)	Sills in black shale	Sills in evaporite	Sills in carbonates
Vøring and Møre (Norway)	85	yes	no	no
Karoo (South Africa)	390	yes	no	no
Amazonas (Brazil)	200	yes	yes	yes
Solimoes (Brazil)	600	yes	yes	yes
Tunguska (Russia)	2000	yes	yes	yes
Sichuan (China)	200	?	?	yes

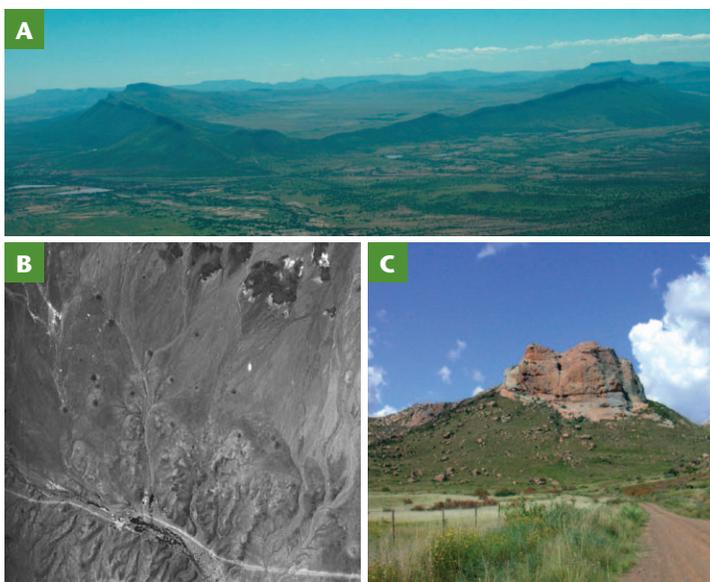


FIGURE 2 Sills and pipes in the Karoo Basin, South Africa. **(A)** The Golden Valley sill complex with its saucer-shaped intrusions (see Polteau et al. 2008). The dolerite sills are about 100 meters thick and were emplaced in sandstones and mudstones. Sill intrusions are associated with all the hills in the background. Photo: Sverre Planke **(B)** Breccia pipes in the Loriesfontein area in the western part of the basin. The pipes are seen as black dots with circular, light grey alteration haloes. A dirt road in the lower half of the image gives the scale. **(C)** The Witkop III hydrothermal vent complex (Svensen et al. 2006) represents an infilled crater formed in the Lower Palaeozoic paleosurface by degassing of fluids released during contact metamorphism deeper in the basin.

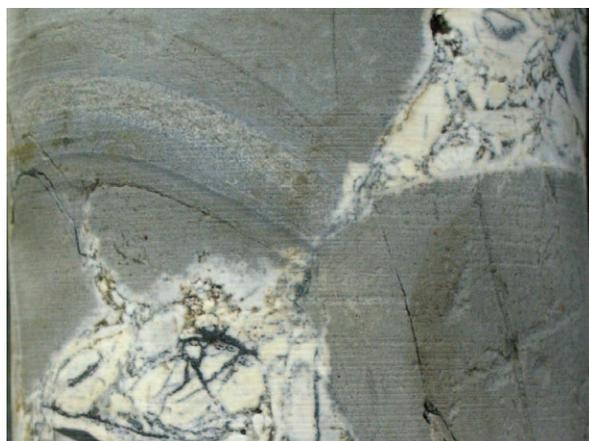


FIGURE 3 Photograph of drill core showing contact metamorphism of black shale in a breccia pipe in the Calvinia area, western Karoo Basin (Svensen et al. 2007). The original shale was black, and contact metamorphism transformed the organic matter into gas, causing a change in color to grey. Secondary bleaching (white) in the sample was caused by reaction with hydrothermal fluids within the breccia and the precipitation of sulfides.

Basin, and the Tunguska Basin (FIG. 1; TABLE 1) (Svensen et al. 2009). In the Siberian Tunguska Basin, spectacular pipes with up to 1.6 km wide subaerial explosion craters formed during the latest Permian. A schematic cross section of a volcanic basin with pipe structures is shown in FIGURE 4. In marine settings, such as the Vøring Basin, the craters can be more than 10 km in diameter (Planke et al. 2005).

SEDIMENT COMPOSITION AND ENVIRONMENTAL EFFECTS

The chemical composition of the sedimentary rocks heated by igneous intrusions has a profound influence on the metamorphic fluid composition (e.g. Svensen et al. 2004, 2009; Ganino and Arndt 2009). An overview of the sediment types heated in various volcanic basins is given in TABLE 2. For example, organic-rich shale generates CH₄ during contact metamorphism, whereas coal generates fluids enriched in CO₂. Both generate water by dehydration. Because many sedimentary basins contained hydrogen-rich kerogen and oil and gas accumulations at the time of sill emplacement, petroleum-derived gases such as CH₄ and C₂H₆ may dominate the metamorphic fluid. If limestones or dolostones are heated, the generated fluid is dominated by ¹³C-enriched CO₂, but if organic matter or graphite is present, the fluid contains ¹³C-depleted CH₄. Evaporites with anhydrite and rock salt can generate SO₂ and HCl, and if organic matter or petroleum is present, CH₄ and halocarbons such as CH₃Cl (methyl chloride) and CH₃Br can also form. Halocarbon generation was recently confirmed by experiments in which natural rock salt from the Tunguska Basin in eastern Siberia was heated to 275°C, to simulate contact metamorphism (Svensen et al. 2009).

In eastern Siberia, a major sill-emplacment event took place at the end of the Permian, when thick sills were injected throughout the basin. Mass-balance calculations suggest that 10,000–30,000 Gt C could have been generated during contact metamorphism of organic matter, accompanied by 4,500–13,000 Gt CH₃Cl (Svensen et al. 2009). The presence of hundreds of pipe structures rooted in evaporitic rocks suggests that the gases were released to the atmosphere. Thus the end-Permian global warming event could have been triggered by aureole degassing. Recent atmospheric modeling showed that >1000 Gt of methyl chloride are required to cause significant stratospheric

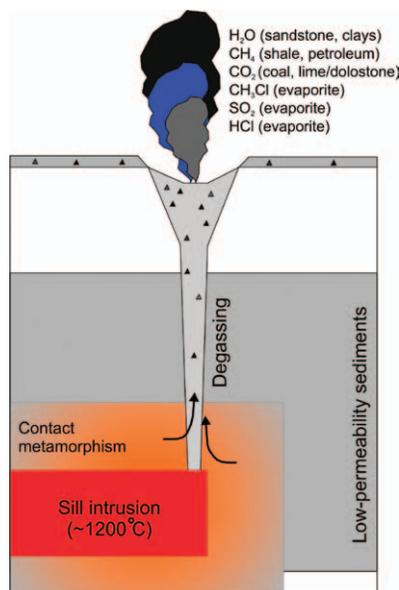


FIGURE 4 Schematic cross section of a sill intrusion with an associated contact aureole and hydrothermal vent complex

ozone depletion over a 100,000-year timescale (Beerling et al. 2007). This may explain the terrestrial end-Permian mass extinctions. Evidence for ozone-layer breakdown and damaging UV-B radiation is found in mutated pollen (Visscher et al. 2004).

CONTACT VERSUS REGIONAL METAMORPHISM

Regional metamorphism is unlikely to cause short-term global climate changes for two main reasons: (1) The timescale of orogeny and crustal extension is long, typically >5 million years, whereas the relevant climatic events occur on a timescale of a few hundred thousand years or less. (2) Regional metamorphism of carbonates generates ¹²C-depleted CO₂, whereas available geological data show that the carbon responsible for Eocene global warming was enriched in ¹²C (e.g. Dickens et al. 1997; Zachos et al. 2001). Contact metamorphism in volcanic basins is a far more likely mechanism for transferring greenhouse gases to the atmosphere on a short timescale. This scenario provides

causal connections between flow processes taking place in the deep interior of the Earth, heat transfer to the shallow crust by rising magma bodies, associated contact metamorphism of carbon-bearing sedimentary rocks, release of massive volumes of greenhouse gases, and associated climate change. In this sequence of events, contact metamorphism represents a critical link that even connects the biosphere to the bowels of the Earth.

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