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## Gas hydrate contribution to Late Permian global warming

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#### ABSTRACT

Rapid gas hydrate release (the "clathrate gun" hypothesis) has been invoked as a cause for the rapid global warming and associated negative carbon isotope excursion observed during the Latest Permian Extinction (LPE). We modeled the stability of gas hydrates through a warming Middle to Late Permian world, considering three settings for methane reservoirs: 1) terrestrial hydrates, 2) hydrates on exposed continental shelves during glacial sea level drop, and 3) hydrates in deep marine settings. Model results show that terrestrial hydrates would rapidly destabilize over  $\sim$ 400 ky after deglaciation for moderate heatflow (40 mW/m<sup>2</sup>), and more rapidly for higher heat flow values. Exposed continental shelves would lose hydrates even more rapidly, after being flooded due to loss of ice storage on land. These two major hydrate reservoirs would thus have destabilized during the Middle to Late Permian climate warming, well prior to the LPE event. However, they may have contributed to the  $>2\%_0$  negative C-isotopic shift during the late Middle Permian. Deep marine hydrates would have remained stable until LPE time. Rapid warming of deep marine waters during this time could have triggered destabilization of this reservoir, however given the configuration of one super continent, Pangea, hydrate bearing continental slopes would have been less extensive than modern day. This suggests that any potential gas hydrate release would have had only a minor contributing impact to the runaway greenhouse during the Latest Permian extinction.

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#### 1. Introduction

The Latest Permian Extinction (LPE), around 252 Ma, was the greatest extinction event in Earth history, with loss of over 90% of marine life (Erwin et al., 2002). Numerous models have been proposed for the cause of extinction, including marine anoxia (Isozaki, 1997; Knoll et al., 1996; Wignall and Hallam, 1992; Wignall and Twitchett, 1996), ocean acidification (Beauchamp and Grasby, 2012; Bertine and Goldberg, 1971; Heydari and Hassanzadeh, 2003; Liang, 2002; Payne et al., 2007), and draw down of bio-essential elements (Grasby and Beauchamp, 2009). Recent work, however, has questioned the global impact of anoxia (Loope et al., 2013; Proemse et al., 2013). Increasingly, there is recognition of a strong correlation between onset of Siberian Trap volcanics and the extinction event (Grasby et al., 2011; Huang et al., 2011; Kamo et al., 2003; Kozur and Weems, 2011; Reichow et al., 2009; Renne et al., 1995; Sanei et al., 2012; Saunders and Reichow, 2009; Shen et al., 2011; Wignall, 2001), supporting original suggestions of a causal relationship (Campbell et al., 1992; Renne and Basu, 1991). Numerous potential devastating impacts of volcanism have been examined, including release of deleterious gases (Black et al., 2012; Ganino and Arndt, 2009; Kontorovich et al., 1997; Svensen et al., 2009), toxic metals (Grasby et al., 2011; Sanei et al., 2012), destruction of the ozone layer (Beerling et al., 2007; Visscher et al., 1996), and combustion of coal and organic rich layers (Reichow et al., 2009; Saunders and Reichow, 2009; Korte et al., 2010; Retallack and Jahren, 2008; Svensen et al., 2009; Grasby et al., 2011; Erwin et al., 2002; Erwin, 1993). Sobolev et al. (2011) also invoke massive degassing related to crustal recycling in the plume head of the Siberian Traps before onset of major eruptions.

The LPE is marked by significant global warming as summarized by Kidder and Worsley (2004). Evidence for warming includes rapid expansion of desert belts (Zeigler et al., 1997), movement of low latitude flora to high latitude locations (Erwin, 1993; Rees et al., 2002; Taylor et al., 1992; Zeigler et al., 1997), and extensive evaporite deposition (Zeigler et al., 1997; Erwin, 1993). Global warming is further supported by stable isotope and other proxies (Georgiev et al., 2011; Joachimski et al., 2012; Luo et al., 2011; Romano et al., 2013; Sun et al., 2012; Yin et al., 2012).

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Global warming has been linked to CO<sub>2</sub> release from Siberian Trap volcanism, however several authors have also invoked rapid greenhouse warming related to massive methane release during the extinction event (Heydari and Hassanzadeh, 2003; Kiehl and Shields, 2005; Ryskin, 2003; Vermeij and Dorritie, 1996; Wignall, 2001). There are two end-members methane sources: (1) methane related to coal combustion (coal bed methane), and (2) release of gas hydrates. In this later case, high CO<sub>2</sub> levels from volcanic emissions (Kidder and Worsley, 2004; Wignall and Hallam, 1993) are thought to have caused global warming that induced dissociation of gas hydrates and release of trapped methane (Dorritie, 2002; Erwin, 1993; Kidder and Worsley, 2004; Racki and Wignall, 2005; Winguth and Maier-Reimer, 2005). It is generally thought that hydrate release would further amplify global warming, destabilize more hydrates, and drive even further warming. This positive feedback system is known as a 'clathrate gun', and is suggested to have the potential to cause a runaway greenhouse over a very short timescale (Kennett et al., 2000, 2003). Such a mechanism has been suggested to have driven warming since the last ice age (Kennett et al., 2000), the Paleocene-Eocene Thermal Maximum (Dickens, 1999; Dickens et al., 1997; Katz et al., 1999), the end-Triassic mass extinction (Ruhl et al., 2011), as well as the LPE event (Krull and Retallack, 2000; Krull et al., 2000). Release of large volumes of methane hydrate have also been invoked to explain the significant negative carbon isotope shift at the LPE (Berner, 2002; de Wit et al., 2002; Erwin, 1993; Gruszcznski et al., 2003; Krull et al., 2004, 2000; Krull and Retallack, 2000; Morante et al., 1994; Sarkar et al., 2003; Twitchett et al., 2001), however, evidence for this has been questioned (Grasby and Beauchamp, 2008; Payne and Kump, 2007; Xie et al., 2007).

Gas hydrate release has been commonly discussed as either an extinction mechanism, or a contributing cause to an extinction. However, there is little knowledge about potential hydrate storage prior to the LPE, or hydrate release rates during the warming Late Permian, that can help constrain these extinction models.

#### 2. Background

Methane is over 20 times more effective in trapping heat in the atmosphere than CO<sub>2</sub> (Archer, 2007; Archer et al., 2008), so that massive hydrate release would cause significant global warming. Methane also has a short atmospheric residence time (Cicerone and Oremland, 1988), as it will quickly oxidize to CO<sub>2</sub>, still causing a global warming affect, albeit lessened. Hydrates form by vertical migration of either thermogenic or biogenic gases that become trapped in sediments within the hydrate stability zone (Kvenvolden, 1993). Ice age periods greatly increase the build up and storage of hydrates through vertical expansion of the stability zone (by lowering subsurface temperatures), as well as through broadening of the regions of permafrost development on the continents (shift of colder climates to lower latitudes) (Kvenvolden, 1993). In addition, during icehouse periods, high-latitude continental shelves are commonly exposed and frozen through lowering of sea level.

Repeated cycles of Gondwana glaciation began around the Mid-Carboniferous ( $\sim$ 320 Ma) (Crowell, 1995). Evidence shows the presence of polar ice caps, and dramatically lowered sea levels during this time (Fielding et al., 2008a, 2008b) that would indicate formation of gas hydrate storehouses under frozen sea and permafrost regions. The worldwide termination of high-order/high amplitude transgressive-regressive sequences (cyclothems) suggests an end to major land ice by the Early Sakmarian (Fielding et al., 2008a; Shi and Waterhouse, 2010). Only more seasonal and/or local glaciations are reported after the Asselian (Shi and Waterhouse, 2010). The last evidence of glacial activity is recorded in Middle Permian sediments in eastern Australia. This glacial event – glacial inter-

val P4 (Fielding et al., 2008a) – may have been linked to global cooling as it is in part contemporaneous with the Kamura cooling event (Isozaki et al., 2007). Evidence of Middle Permian cooling can also be observed in the Sverdrup Basin (Arctic Canada) along the NW margin of Pangea (Beauchamp and Baud, 2002; Beauchamp and Grasby, 2012). Permafrost soils were also documented in southern high latitudes (Retallack, 1999) in the early part of the Late Permian.

The Middle to Late Permian was a time of rapid change from icehouse to greenhouse which predates the latest Permian-Early Triassic shift to hothouse conditions (Kidder and Worsley, 2004). This trend is shown by disappearance of Gondwana glaciers, desertification of low to mid latitude areas, and forestation and accumulation of coal measures at high latitudes (Crowell, 1995; Erwin, 1993; Kidder and Worsley, 2004; Taylor et al., 1992; Zeigler et al., 1997). Late Permian paleosols in Australia show a change from present-day soil characteristics of 68-70°S, to those more characteristic of latitudes ~40-58°S (Retallack, 1999). Furthermore, Retallack and Krull (1999) show evidence of high latitude deeply weathered Late Permian paleosols. Korte and Kozur (2010) also show the presence of ferns and other fauna that indicate the lack of permafrost soils in the Late Permian Siberian Trap area. This warming trend is supported by climate models of Kiehl and Shields (2005) and Rampino and Caldeira (2005).

The Late Permian warming would have primarily affected Pangea's polar regions. Permafrost would degrade with the disappearance of glacial ice, as observed in the present-day and since the last glacial maximum (Lawrence and Slater, 2005), and initiate methane release. Warming and ice melting would have also caused changes in sea level, which along with other eustatic sea level drivers, would have affected hydrate stability. A rise in sea level would increase trapping of gas hydrates due to pressure build up, reducing the impact of warming on hydrate destabilization.

Using modeling techniques developed to assess the rate of dissociation of modern hydrates, we here assess the role of methane hydrate-release on global warming and isotopic shift observed in global exogenic carbon reservoirs across the stratigraphic interval that recorded the largest mass extinction in Earth history.

### 3. Methods

Depending on the environment of occurrence, gas hydrates will respond differently during a waning icehouse. We consider three hydrate environments: (1) onshore hydrates (terrestrial permafrost bound hydrates), (2) offshore hydrates (hydrates developed on exposed marine shelves during icehouse sea-level lowstands that are subsequently flooded by marine transgression), and (3) marine hydrates (deep water hydrates formed in the sea bed that is never exposed to the atmosphere).

Terrestrial hydrates are the simplest case, where warming air temperatures transfer heat into the ground, progressively warming and melting permafrost. During glaciation sea levels drop due to water storage, as ice, on land. During such time gas hydrates can form on shelf areas exposed to freezing air temperatures. Although exposed to similar amplitude of surface warming, as with the terrestrial case, the post-glacial ground warming and associated permafrost and gas hydrate decay on continental shelves are complicated by sea level rise and flooding of the shelves after the end of the glacial period.

Marine offshore hydrate deposits typically occur in the first hundreds of metres of sediment (Ruppel, 2011). During post-glacial warming, the glacial-interglacial temperature variation of deep bottom waters are supposed to be smaller than that considered for the terrestrial or flooded shelves cases. The present temperatures of deep bottom waters are in the range 2 to 5 °C, and during the glacial period could not be below -1 °C, which means a max-

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