A volcanic trigger for the Late Ordovician mass extinction? Mercury data from south China and Laurentia

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ABSTRACT
The Late Ordovician mass extinction (LOME), one of the five largest Phanerozoic biodiversity depletions, occurred in two pulses associated with the expansion and contraction of ice sheets on Gondwana during the Hirnantian Age. It is widely recognized that environmental disruptions associated with changing glacial conditions contributed to the extinctions, but neither the kill mechanisms nor the causes of glacial expansion are well understood. Here we report anomalously high Hg concentrations in marine strata from south China and Laurentia deposited immediately before, during, and after the Hirnantian glacial maximum that we interpret to reflect the emplacement of a large igneous province (LIP). An initial Hg enrichment occurs in the late Katian Age, while a second enrichment occurs immediately below the Katian-Hirnantian boundary, which marks the first pulse of extinction. Further Hg enrichment occurs in strata deposited during glacioeustatic sea-level fall and the glacial maximum. We propose that these Hg enrichments are products of multiple phases of LIP volcanism. While elevated Hg concentrations have been linked to LIP volcanism. While elevated Hg concentrations have been linked to LIP volcanism, we analyze samples from successions in south China and Laurentia spanning the interval of the LOME and Hirnantian glacial maximum (Fig. 1).

INTRODUCTION
Paleoclimate records indicate global cooling during ~35 m.y. of the Early and Middle Ordovician, a relatively stable climate in the ~8-m.y.-long Katian Age, and a glacial maximum in the Hirnanrtian Age (445.2–443.8 Ma) (Trotter et al., 2008; Finnegan et al., 2011; Melchin et al., 2013). Cooling likely resulted in the establishment of ice sheets on polar Gondwana in the Katian Age or even earlier (Saltzman and Young, 2005; Finnegan et al., 2011; Pohl et al., 2016). The subsequent rapid expansion of Hirnantian ice sheets resulted in glacioeustatic sea-level fall and decreased temperatures (Finnegan et al., 2011) associated with the first pulse of the Late Ordovician mass extinction (LOME) (Melchin et al., 2013). The second pulse of the LOME occurred as glaciers melted, oceans warmed, and anoxic seawater transgressed the shelves (Melchin et al., 2013). The cause of the glacial advance is unknown, but has been attributed to CO₂ levels falling below a critical threshold (Herrmann et al., 2004). Lefebvre et al. (2010) used a coupled biogeochemical-energy balance model to demonstrate that chemical weathering of a hypothetical late Katian large igneous province (LIP) could have lowered CO₂ over millions of years to cause major ice sheet growth. However, geological and geochemical evidence of such an eruption are currently lacking, and it is unclear if the apparent rapid time scale of the Hirnantian glacial advance is consistent with a weathering mechanism.

Phaneroozoic mass extinctions have been linked geochronologically and mechanistically to the emplacement of LIPs (Courtillot and Renne, 2003; Bond and Wignall, 2014). CO₂ release associated with LIP emplacement can produce greenhouse warming, ocean acidification, and marine anoxia (Self et al., 2014), and SO₂ release can induce short-term cooling through the production of stratospheric sulfur aerosols (Schmidt et al., 2015). Volcanism is the major preanthropogenic source of mercury to Earth’s surface environments (Selin, 2009), and the accumulation of Hg in sediment can be used as a proxy for ancient volcanic events (Sanei et al., 2012; Font et al., 2016; Thibodeau et al., 2016). The atmospheric residence time of Hg is long (~1–2 yr) (Selin, 2009) relative to atmospheric mixing time, and volcanicogenic Hg can accumulate globally (Schuster et al., 2002). Because Hg binds to organic matter in marine settings, Hg concentration can produce greenhouse warming, ocean acidification, and marine anoxia (Self et al., 2014), and SO₂ release can induce short-term cooling through the production of stratospheric sulfur aerosols (Schmidt et al., 2015). Volcanism is the major preanthropogenic source of mercury to Earth’s surface environments (Selin, 2009), and the accumulation of Hg in sediment can be used as a proxy for ancient volcanic events (Sanei et al., 2012; Font et al., 2016; Thibodeau et al., 2016). The atmospheric residence time of Hg is long (~1–2 yr) (Selin, 2009) relative to atmospheric mixing time, and volcanicogenic Hg can accumulate globally (Schuster et al., 2002). Because Hg binds to organic matter in marine settings, Hg concentration

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At Wangjiawan in south China, dark shale of the Wufeng Formation was deposited on an anoxic deep shelf facing the open ocean (Chen et al., 2006) (Fig. 2A). The overlying shaley limestone of the Kuanyinchiao Formation was deposited during shallowing; these strata represent the transition to cool-water carbonate deposition and host the Hirnantia fauna characteristic of the glacial maximum (Chen et al., 2006). The overlying Lungamachi Formation represents postglacial flooding of the basin (Chen et al., 2006). At the Monitor Range (Nevada, USA) of western Laurentia, the lower Hanson Creek Formation consists of dark lime mudstone deposited below wave base; limestone of the upper Hanson Creek Formation was deposited in progressively shallower environments with an exposure surface succeeded by deepening at the top of the succession (Finney et al., 1997) (Fig. 2B). Both successions contain the globally recognized Hirnantian positive carbon isotope excursion (Gorjan et al., 2012; Jones et al., 2016), and both have a chronostratigraphic framework provided by graptolite biostratigraphy (Finney et al., 1997; Chen et al., 2006) (Fig. 2). The Monitor Range section includes the ornatus graptolite zone, which precedes the oldest samples from Wangjiawan. The sample sets analyzed here are the same as those described in Jones et al. (2016) for the Monitor Range and in Gorjan et al. (2012) for Wangjiawan.

Carbonate content of whole-rock powders was determined by mass loss following decarbonation with hydrochloric acid. Carbon content of insoluble residue was measured with a Costech ECS 4010 elemental analyzer. The relative standard deviation of TOC measurements was <4.5%.

Whole-rock powders were analyzed for Hg with a Teledyne Leeman Labs Hydra IIc mercury analyzer with relative standard deviation <10%.

**RESULTS**

At Wangjiawan (Fig. 2A), Hg and Hg/TOC rise above background levels in the upper pacificus zone, immediately below the first pulse of mass extinction and initiation of shallowing. A second enrichment in Hg begins in shales immediately below the base of the Kuanyinchiao Formation and persists through the shallow-water facies; Hg/TOC reaches ~10× background levels before declining toward baseline just below the Lungamachi Formation.

At the Monitor Range (Fig. 2B), samples with enriched Hg and Hg/TOC occur in the ornatus zone in the lower ~60 m of the section. They are succeeded by samples with low background Hg and Hg/TOC through the upper ornatus and lower pacificus zones. The upper pacificus zone is marked by extreme Hg and Hg/TOC enrichments in two limestone samples that reach ~500× background. Based on graptolite and δ¹³C chemostratigraphy, the Hirnantian sediment accumulation rate at the Monitor Range is ~80× higher than at Wangjiawan, allowing for sampling at much higher temporal resolution at the Monitor Range. Hirnantian strata contain a series of pulsed Hg anomalies that are ~5–10× higher than the ~6 ppm background.

**DISCUSSION**

The stratigraphic enrichments in Hg and Hg/TOC may have been controlled by a number of factors, including changes in organic matter...
content, early diagenetic degradation of organic matter, and enhanced environmental Hg loading. The absence of a strong correlation between Hg and TOC concentrations in the Monitor Range data ($r^2 < 0.01$; Fig. DR1 in the GSA Data Repository) suggests that the stratigraphic pattern of Hg concentration is not solely an artifact of changing TOC content. Although a correlation exists at Wangjiawan, TOC content alone cannot explain all the variability in Hg concentration ($r^2 = 0.53$; Fig. DR1). Because TOC content is commonly lowered during early diagenesis, Hg/TOC ratios have the potential to be diagenetically inflated; this is of particular concern for samples with low TOC. Therefore, we code Hg/TOC data by TOC concentration in Figure 2. The *ornatus* zone Hg/TOC anomaly at the Monitor Range is carried by samples with high (>0.2 wt%) and moderate (0.10–0.20 wt%) TOC content, with concomitant enrichment in absolute Hg concentration (Fig. 2B); these observations support an interpretation of enhanced environmental Hg loading in the latest Katian. The upper *pacificus* zone Hg and Hg/TOC enrichments at both sections differ greatly in magnitude but occur at the same stratigraphic position. At Wangjiawan the upper *pacificus* anomaly is marked by a twofold increase in Hg/TOC and a fourfold increase in Hg concentration above background levels, all in samples with high TOC values (Fig. 2A). Although at the Monitor Range this anomaly is carried by low TOC samples (<0.10 wt% TOC; Fig. 2B), the extreme enrichments in Hg concentration (as high as 500× background levels) are most parsimoniously explained by high environmental fluxes. While a diastem could produce such enrichment, field evidence for a hiatus at this stratigraphic position is lacking (Finney et al., 1997). Hirnantian strata at Wangjiawan contain anomalies in both Hg and Hg/TOC, although the three highest Hg/TOC values are carried by samples with moderate TOC (Fig. 2A). Hirnantian strata at the Monitor Range include samples with Hg concentrations as much as 10× above background levels, suggesting enhanced environmental loading, but low TOC content makes the elevated Hg/TOC values more difficult to interpret.

We argue that the Hg enrichments observed in both sections are the products of enhanced environmental loading caused by LIP emplacement. The sedimentological and stratigraphic context of LIP-generated Hg anomalies may provide insights into Hirnantian glaciation and the LOME. The upper Katian *ornatus* zone anomaly at the Monitor Range (Fig. 2B) is ~1.5–4.0 m.y. older than the start of the Hirnantian (Finney et al., 1997). Lefèvre et al. (2010) modeled the consumption of atmospheric CO$_2$ by emplacement and weathering of a LIP in the late Katian and showed that 5 °C of cooling could occur in 2 m.y., the result being sensitive to the rate, volume, and paleolatitude of LIP emplacement. Our *ornatus* zone Hg data provide indirect geochemical evidence for such a late Katian volcanic event, and we suggest that attendant cooling changed climatic boundary conditions (Finnegan et al., 2011) such that subsequent eruptions had catastrophic effects on climate.

Further LIP emplacement broadly synchronous with the Hirnantian glacial maximum is suggested by Hg records at both sections (Fig. 2). Volcanic SO$_2$ emission produces sulfur aerosols that can affect climate by increasing planetary albedo upon reaching the stratosphere (Robock, 2000). Global cooling from the weathering of basaltemplaced during an *ornatus* zone eruption would have lowered the tropopause, increasing the likelihood that subsequent eruptions would deliver radiatively active sulfur aerosols to the stratosphere (Macdonald and Wordsworth, 2017). We suggest that rapid expansion of preexisting ice sheets was induced by an albedo catastrophe initiated by a second phase of eruptions represented by the upper *pacificus* zone Hg anomaly. Expanded ice cover was possibly maintained by eruptions throughout the Hirnantian (Fig. 2), facilitated by the positive feedback between cooling and volcanic aerosol injection above the tropopause (Macdonald and Wordsworth, 2017). Because SO$_2$ must be injected into the stratosphere on a decadal time scale to affect climate (Schmidt et al., 2015), this mechanism would require short hiatuses between eruptions to fully account for the duration of the glacial maximum; estimates for time between flows of the Deccan Traps and Columbia River flood basalts range widely, from 10 to 1000 yr (Self et al., 2014). However, a cascade of environmental change including ice albedo feedback and changes in ocean circulation may have instead maintained the ice extent on longer time scales than the radiative forcing that initiated the ice advance.

Albedo-driven cooling would need to counteract any warming from CO$_2$ release associated with LIP emplacement, which has been identified as a potential contributor to the Permian-Triassic extinction (e.g., Sun et al., 2012). However, the volume and rate of volcanic CO$_2$ released during LIP emplacement may be low (Self et al., 2014) and may occur only after an initial phase of SO$_2$ release due to progressive thermal erosion of the lithosphere (Guex et al., 2016). Furthermore, a critical difference for ice sheet response between the LOME and Permian-Triassic extinction is the existence of a cool climate with preexisting ice cover in the Late Ordovician (Finnegan et al., 2011). Ice expansion at the beginning of the Hirnantian would have been amplified by ice albedo feedback, whereas the warm ocean and continents lacking ice in the late Permian would have hindered the establishment and expansion of ice sheets. Nevertheless, an albedo cooling scenario similar to the one presented here has been proposed for the Permian-Triassic extinction based on high-resolution U/Pb dating of a global marine regression at the boundary and extinction level (Baresel et al., 2017).

Because albedo changes have an instantaneous effect on planetary energy balance, a volcanic trigger could explain the apparent rapidity of the Hirnantian glacial expansion and temperature decline. It may also explain the severity of the first pulse of mass extinction, because marine taxa would have had little opportunity to adapt or migrate to more favorable environments. Late Hirnantian warming from CO$_2$ release during the later phases of LIP emplacement in concert with a reduction of SO$_2$ emissions (Guex et al., 2016) may have ultimately caused deglaciation as aerosol albedo forcing waned. The second phase of the LOME is associated with warming, marine transgression, and anoxia (Melchin et al., 2013), all of which are hallmarks of the global environmental effects of LIP-associated CO$_2$ (Self et al., 2014).

A late Katian–Hirnantian LIP has not yet been identified. However, Ordovician basalts, including the Sierra del Tigre in Argentina (González-Menéndez et al., 2013), the Suordakh in eastern Siberia (Khudeley et al., 2013), and the Cape St. Mary’s sills in Newfoundland (Greenough et al., 1993) (Fig. 1A), have loose age constraints that may be compatible with Hirnantian volcanism once they are precisely dated.

CONCLUSION

We document three Hg enrichments associated with the LOME and suggest that they are markers of LIP volcanism. While specific mechanisms linking LIP volcanism to the LOME and Hirnantian glacial maximum are speculative until direct geological and geochronological evidence of a late Katian–Hirnantian LIP is found, the stratigraphic position of the oldest of the Hg anomalies is consistent with modeling predictions linking the chemical weathering of a Katian LIP to Late Ordovician cooling. If the Hg enrichments just preceding the Katian–Hirnantian boundary and through the Hirnantian glacial maximum represent further LIP activity, the synchronous volcanism and glacial expansion may be reconcilable through the albedo effects of volcanic sulfate aerosols. If confirmed, the LIP inferred from our Hg data would join those associated with mass extinction events throughout the Phanerzoic and strengthen the case for LIP volcanism as a primary driver of the environmental changes that caused mass extinction of life on Earth.

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1GSA Data Repository item 2017205, geochemical data and cross plots, is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.