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EASome Geoscientists Are Concluding that Organic Enrichment of Rock is by Volcanic Ash Fall. The Implications Are Dramatic; But Are They Probable?*

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Abstract

Zimmerle (1985) and Parker (2017) concluded that all organically enriched rocks are the result of volcanogenic input; direct ash fall and redeposition of ash fall minerals. Lee et al. (2018) wrote that volcanic ash was a driver of carbon burial in the Cretaceous. Frebourg et al. (2016) examined outcrops of the Boquillas-Eagle Ford and concluded that the cyclicity of organic enrichment, and those nutrients causing organic enrichment were from volcanic ash fall. Sonnenfeld et al. (2016) found “hundreds” of layers of volcanic ash in the organically enriched Niobrara Formation. For ash to be the key to organic enrichment (1) a connection must exist between Oceanic Anoxic Events (OAEs) and voluminous ash fall and, (2) altered ash must largely be un-quantified in sedimentary rocks. Ross et al. (2005) observed “the near-ubiquitous occurrence of mafic volcaniclastic deposits as an integral component in large igneous provinces.” “Mafic volcaniclastics make up a significant fraction of large igneous province eruptive volume” (Ukstins-Peate et al., 2015). “The volcaniclastics in flood basalts may be the major missing link between flood basalts and extinctions” (Ukstins-Peate et al., 2015). The complexity of diagenetic alteration can be appreciated in this description of a tuff from the Eocene Green River Shale. “The Mahogany Marker Tuff consists of authigenic sodium feldspar, analcime, quartz, ankerite, dolomite, potassium, feldspar, calcite with lesser amounts of siderite, hematite, pyrite, undifferentiated clays, pyrrhotite, biotite, marcasite, and locally dawsonite (Mason, 1983). Volcanogenic rocks “hidden” in plain sight include quartz sand and mud (Smyth et al., 2003), chert (Wadia, 2007; Chatellier, 2015), bauxite deposits (Isphording et al., 1995), hematite in red beds (Kruiver et al., 2000), and chamosite in oolitic iron ore (Ulf Sturesson, 1992). Jurassic uranium ore is leached from ash (Falkowski, 1979) as is Eocene uranium in Gulf Coast sediments (Hall, 2013). Trona ($NaCO_3$) of the Green River Shale and in Turkey is an evaporative mineral from ash fall alteration (Turkey -- Helvaci, 2010). Volcanogenic rocks are part of OAEs and their alteration minerals are much more diverse than just bentonites and tonsteins.

Introduction

Despite years of study, modeling, and speculation, geoscience has not reached a consensus on a consistent mechanism to form organically enriched rocks. Wagner et al. (2014) summarized the situation this way; “The causal and genetic relationships controlling the timing, composition, and internal variability of these marine OC-rich {organic carbon rich – DMP} shale over large distances and during variable global climate states are still far from understood.”

A mechanism is gaining interest that does not include, a) nutrient rich upwelling, b) ocean stratification leading to widespread anoxia or, c) increased climate-driven seasonality that leads to increased primary productivity. Zimmerle (1985) and Parker (2017) have concluded that all organically enriched rocks are the result of volcanogenic input; both by direct ash fall and redeposition of ash fall minerals. Other authors have come to similar conclusions but limited them to certain geologic time periods or particular rock formations. Lee et al. (2018) concluded that volcanic ash was a driver of carbon burial in the Cretaceous. Frebourg et al. (2016) examined outcrops of the Boquillas-Eagle Ford system and concluded that the cyclicity of organic enrichment, and those nutrients that caused organic enrichment, were from volcanic ash fall. Sonnenfeld et al. (2016) found “hundreds” of layers of volcanic ash in the organically enriched Niobrara Formation when he examined it for mechanical properties. Peng et al. (2015) and Li (2013) concluded that ash was an important factor in creating organic enrichment in shale and tight oil plays.

The “Volcanic Tephra Fall (VTF)” mechanism for forming organically enriched rocks is a variation of the following mechanism: Ash fall fertilizes the water column and increases primary productivity. The organic matter descends to the seafloor where it is rapidly buried by more ash. If the ash is thick enough, it creates transient seafloor anoxia and prevents the biodegradation of the organics (Parker, 2017). The ash then diagenetically alters, forming a variety of minerals and clays.

The hypothesis that volcanic ash fall might always be the driver of organically enriched rock formation requires significant changes in the way we think about sedimentary rock. There are corollaries that “also-must-be-true” for VTF to consistently be the enriching mechanism.

Two “also-must-be-true” corollaries are, (1) there must be a direct connection between those times when more organically enriched rocks formed, Oceanic Anoxic Events (OAEs), and voluminous, or more frequent, volcanic ash fall and, (2) volcanic ash must make up a much larger percentage of the sedimentary rock mass than presently recognized. For ash to trigger the formation of large volumes of organically enriched rocks, large volumes of altered ash must also exist in non-organically enriched rocks. As an example of why this must be true, during large scale ash fall events, ash would also fall on dry land where no phytoplankton bloom would occur.

Methods

A search of the published literature supports the thesis that sizable, largely unrecognized volumes of volcanic ash has fallen episodically in earth’s history. This new paradigm explains what is observed at times of Oceanic Anoxic Events better than other existing theories, such as those including the upwelling of nutrient-rich water, reduced oceanic circulation causing anoxia, and increased seasonality causing enhanced primary productivity. This discussion addresses whether this new paradigm could apply to all OAEs.

Results – Corollary One

A direct connection between organic enrichment and Large Igneous Province (LIP) emplacement exists (Figure 1). The temporal link between LIPs and oceanic anoxic events (and extinctions) is recognized (Figure 2). Bond et al. (2014) identified several extinction crises that showed the best correlation with mass volcanism: the Frasnian-Famennian (Late Devonian), Capitanian (Middle Permian), end-Permian, end-Triassic, and Toarcian (Early Jurassic) extinctions.

The relationship between emplacement of LIPs and volcanic tephra fall is described by Ross et al. (2005). He observed "the near-ubiquitous occurrence of mafic volcaniclastic deposits as an integral component in large igneous provinces." "Mafic volcaniclastics make up a significant fraction of large igneous province eruptive volume, including in the Siberian {Permian-Triassic Boundary Anoxic Event ~252 Ma – DMP}, Emeishan {just prior to Permian-Triassic Boundary Anoxic Event and a probable contributor ~265 Ma – DMP}, North Atlantic Igneous Province {NAIP ~ 60.5 to 54.5 Ma and probable contributor to Paleocene-Eocene Thermal Maximum PETM – DMP}, Karoo and Ferrar (Ukstins-Peate et al.,, 2015). {NOTE: Karoo and Ferrar at 183 Ma likely contributor to Early Jurassic Pliensbachian-Toarcian Anoxic Event – DMP}."

The huge volume of volcaniclastics that can be associated with LIP emplacement is documented for the Siberian Flood Basalts that are recognized as the probable trigger for the earth's most dramatic extinction event, that at the Permian – Triassic boundary (252.6 Ma). Ukstins-Peate et al. (2015) describe volcaniclastic deposits associated with the Siberian Flood Basalts. "Along almost 200 km of the Angara River the river cliffs consist of volcaniclastics, and visible outcrops are as much as 250 m thick." "Similar deposits occur along 200 km of the Nizhnaya Tunguska River, stretching east–west past the middle Siberian town of Tura. In Tura, drill cores indicate at least 500 m of tuffs transitioning to overlying effusive lavas (Drenov, 1985). These drill cores demonstrate the voluminous phreatomagmatism immediately preceded the main stage of effusive lava emplacement."

Ukstins-Peate et al. (2015) were the first to state, "The volcaniclastics in flood basalts, therefore, may be the major missing link between flood basalts and extinctions."

The relationship Ross et al. (2005) and Ukstins-Peate et al. (2015) describe is direct; the volcaniclastic rocks are immediately associated with, and causally related to, emplacement of an igneous province. But when the earth's plates are realigning themselves in such a way as to extrude large volumes of lava and volcaniclastics, additional source areas for volcaniclastics are likely in arc-related zones distant from the LIP.

Some LIPs, such as the Deccan Traps of northern India (Cretaceous/Paleogene Boundary) are recognized to have fewer Mafic Volcaniclastic Deposits (MVDs) than other LIPs. However, a description of a classic outcrop section illustrates that there is much evidence for volcaniclastics from other sources at that time. The Cretaceous-Paleogene (K-P) boundary is preserved in coal-bearing, fluvial rocks in the lower Raton Formation (Late Cretaceous and Paleocene) at several sites in the east-central Raton Basin (southern Colorado and New Mexico, USA). The K-P boundary occurs at the top of a kaolinitic claystone layer, commonly referred to as the "boundary clay layer," in an interval of coal and carbonaceous shale (both formed by ash; Parker, 2017). The bulk mineralogy of the boundary clay bed (mainly well crystallized kaolinite) is similar to that of other kaolinite-rich clay beds (tonsteins) that altered in coal swamps from airfall volcanic ash. (Pollastro et al., 1987).

Volcanic ash has been concluded to be the driver of carbon burial during the Cretaceous (Lee et al., 2018).

Discussion – Corollary One

Conclusion on Corollary One: There is substantial evidence that times of LIP emplacement and OAEs are also times of large scale and frequent volcanic ash fall; not only mafic ash fall directly associated with LIP emplacement, but also explosive arc volcanism associated with tectonic plate movements. More frequent and larger quantities of volcanic tephra have likely fallen at those times of LIP emplacement, OAEs, and extinctions, than at other times in the Phanerozoic.

Results – Corollary Two

The mechanism to create organic shale from volcanic ash includes the stimulation of phytoplankton blooms by ash fall. At those times ash fall also would occur on dry land where there could be no phytoplankton bloom. For organically enriched shales to be formed with volcanic ash, non-organically enriched shale and other sedimentary rocks would also have large amounts of alteration products of fallen volcanic ash. These alteration products of ash in non-organically enriched rocks must be largely unrecognized and unquantified. Is it probable that volcanogenic minerals make up a much larger portion of the sedimentary rock mass than currently recognized?

Scudder (2015) noted that much altered volcanic ash is not in discrete, measurable layers, but is instead dispersed in shale and has not been studied or quantified.

Altered volcanic tephra can be much more than those thin layers of bentonites and tonsteins geoscience readily recognizes. The complexity of diagenetic alteration of exploded volcanic tephra can be appreciated in the following description of a tuff from the Eocene Green River Shale. “The Mahogany Marker Tuff consists of authigenic sodium feldspar, analcime, quartz, ankerite, dolomite, potassium, feldspar, calcite with lesser amounts of siderite, hematite, pyrite, undifferentiated clays, pyrrhotite, biotite, marcasite, and locally dawsonite. Analcime is not present in all samples and in samples that are analcime-free, K-feldspar shows a greater abundance. Dawsonite is locally present only in analcime-free samples. The presence or absence of analcime and K-feldspar is attributed to the geochemical conditions that existed in the lake at the time of deposition of the Mahogany marker.” (Mason, 1983).

Besides those minerals mentioned by Mason as part of the Mahogany Marker Tuff, volcanogenic rocks “hidden” in plain sight include quartz sand and mud (Smyth et al., 2003), layers of chert (Wadia, 2007; Chatellier, 2015), bauxite deposits (Isphording et al., 1995), hematite in red beds (Kruiver et al., 2000), chamosite ooids in oolitic iron ore (Sturesson, 1992), and volcanic accretionary lapilli from 3.4 billion year old rocks which were originally interpreted as carbonate ooids (Lowe et al., 1978). Jurassic sedimentary uranium is leached from ash (Falkowski et al. 1979) as is Eocene uranium in sediments of the Gulf Coast (Hall, 2013). Trona ($NaCO_3$) of the Green River Shale and Beypazari, Turkey, is an evaporative mineral resulting from ash fall alteration (Turkey -- Helvaci, 2010).

Discussion – Corollary Two

It is clear that exploded, altered tephra exists in sedimentary rock in minerals other than layered bentonitic and kaolinitic clays. Because of the diversity of the alteration products of exploded volcanic tephra, it is very probable that geoscience has not adequately quantified them.

After years considering the interaction of climate-induced high biologic productivity, ocean stratification with anoxia, and transgressive seas, the lack of geoscientific consensus on a mechanism(s) for black shale formation implies that another reasonable mechanism should be considered. Volcanic ash is a large part of LIP emplacement volume that can be coincident with OAEs, when more black shale forms. When tectonic plates are moving related to LIP emplacement, arc volcanism can contribute additional falling volcanic tephra.

Conclusion

There is a documented direct connection between volcanic tephra fall and LIP emplacement. The diversity of minerals that are alteration products of ash make it likely that the volume of volcanogenic minerals in sedimentary rocks is much greater than currently recognized.

Volcanic ash fall is likely to be the "Smoking Gun" linking LIP emplacement to OAEs, and to organically enriched rocks.

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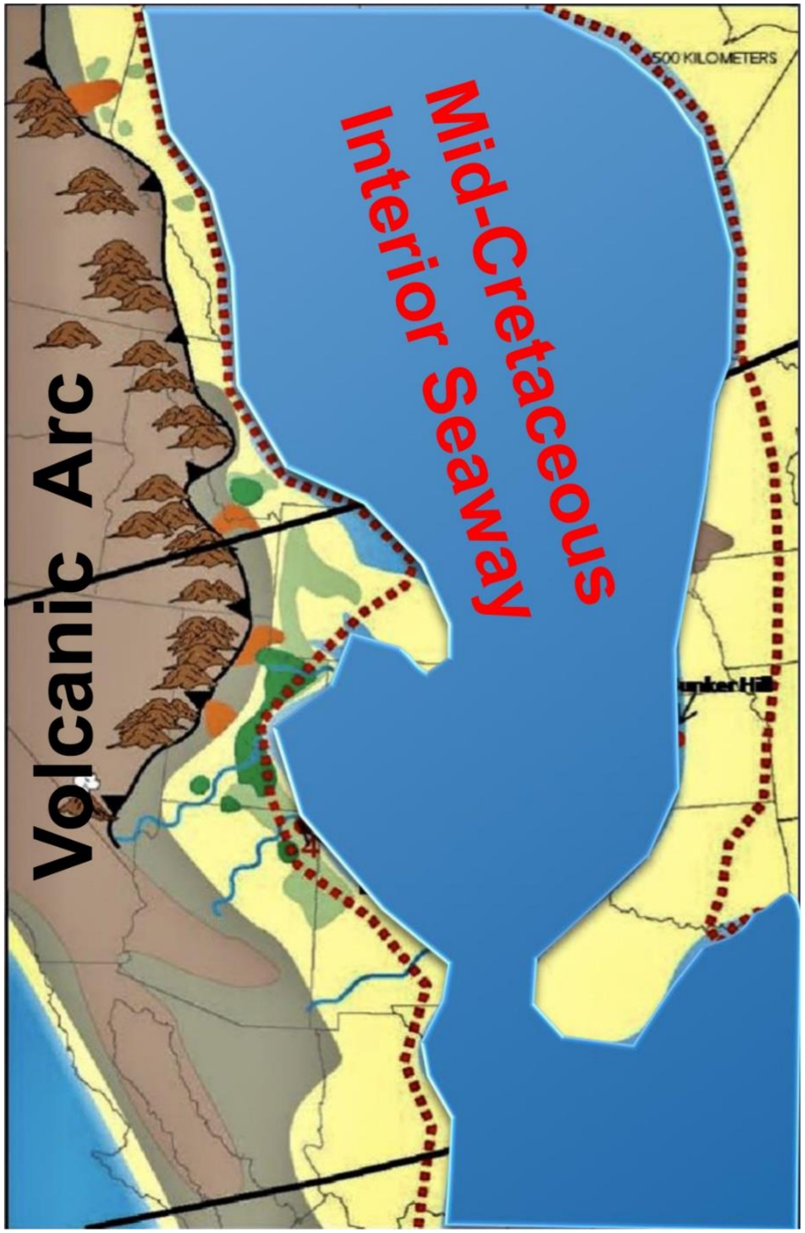

Figure 1. In North America, compounding the effects of global LIP volcaniclastics was ash from an active volcanic arc west of the Interior Seaway. Volcanism extended from Triassic to Late Cretaceous peaking in the Cenomanian (95 Ma) and Campanian-Maastrician boundary (75 Ma) (Christianson et al., 1994). {And episodically through the Oligocene - DMP}. Drawing Modified From: Shang, et al., 2018.

Age	Large Igneous Province	Reference
PETM	No. Atl. Ign. Prov.	Dickson et al (2015)
Cret/Pal.	Deccan Traps	V. Courtillot et al (1986)
Cen/Tur.	Caribb. LIP/Hi-Arctic LIP	C. Shroder-Adams et al (2019)
Early Aptian	H.Arctic LIP; Ontong Java Pl.	Corfu (2013); Zorina (2017)
Trias/Juras.	Central Atl. Magm. Prov.	Marzoli et al. (2004)
Permo-Triassic	Siberian + Tungass Traps	Renne (1995) & Hong (2011)
Late Dev/Carb.	Kola & Timon-Pechura magm.	Bond-Wignall (2014)
End Ord.	Mercury anomalies indicate LIP	Sell (2013) Jones (2017)

Figure 2. The emplacement of Large Igneous Provinces (LIPs) is the recognized “Trigger” for Oceanic Anoxic Events and the Paleocene-Eocene Thermal Maximum (PETM).