PSVolcanic Ash Fall - The Key to Organic Rich Shale and Coal Formation*

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Abstract

Volcanic ash fall is the most important cause for the existence and preservation of organic rich shales. If this hypothesis is confirmed, the implications are many. Formation of organic-rich shales correlates with high water column productivity rather than anoxia. Coastal upwelling occurs in about one percent of the world's oceans today. Upwelling concentrates sediments locally or regionally and does not adequately explain thin shale laminations extending across large percentages of particular sedimentary basins. Cretaceous organic rich shales were induced by an undefined mechanism associated with massive volcanic events. Ash fall causes a phytoplankton bloom and, potentially, temporary sea floor anoxia. Ash fall has been concluded to cause the organic richness of many tight oil plays and at least one Triassic lacustrine shale. Organic rich shales and coals possess many layers of bentonites and tonsteins. Hundreds of thin layers of volcanic ash have been documented in the Niobrara shale, all below electric log resolution. Sixty-five layers of volcanic ash have been documented in the Paleocene Big Dirty coal bed. The Eagle Ford contains abundant ash beds of varying thickness rich in planktonic foraminifera, indicating that high production may be triggered by nutrient flux associated with ash fall. Extrapolating from the Smithsonian Global Volcanism database, 11,700 eruptions of VEI 6 or greater (Krakatoa) could have occurred worldwide during a 3 million year depositional period for the Eagle Ford shale. Cores through productive shales should be analyzed for thin volcanic ash layers and their weathered remnants intermingled with other sediments.

References Cited

Bloch, S., and K.S. Johnson, 1980, Distribution and Alteration of Ogallala Volcanic Ash Deposits and Their Possible Relation to Uranium Mineralization in Western Oklahoma: AAPG Bulletin, v.64/5, p. 677-678.

Blumenberg, M., and F. Wiese, 2012, Imbalanced nutrients as triggers for black shale formation in a shallow shelf setting during the OAE 2 (Wunstorf, Germany): Biogeosciences v.9, p. 4139-4153. DOI: 10.5194/bg-9-4139-2012.

Bohor, B.F., and D.M. Triplehorn, 1984, Accretionary Lapilli in Altered Tuffs Associated with Coal Beds: Journal of Sedimentary Petrology, v.54/1, p.

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Bohor, B.F., and D.M. Triplehorn, 1993, Tonsteins: Altered Volcanic-Ash Layers in Coal-Bearing Sequences: Geological Society of America Special Papers, v. 285, p. 1; DOI: 10.1130/SPE285-p1

Bond, D.P.G., and P.B. Wignall, 2014, Large igneous provinces and mass extinctions; An update: in G. Keller and A.C. Kerr (eds), Volcanism, Impacts, and Mass Extinctions: Causes and Effects, GSA Special Paper 505, p. 36-55.

Briffa, K.R., P.D. Jones, F.H. Schweingruber, and T.J. Osborn, 1998, Influence of volcanic eruptions on Northern Hemisphere summer temperature over the past 600 years: Nature v. 393, p. 450-455; DOI: 10.1038/30943

Calvert, S.E., R.E. Karlin, L.J. Toolin, D.J. Donahue, J.R. Southon, and J.S. Vogel, 1991, Low organic carbon accumulation rates in Black Sea sediments: Letters to nature: Nature, v. 350, p. 692-695, DOI:10.1038/350692a0

Connor, C.W., 1985, Sixty-Five Volcanic Events Recorded in Single Coal Bed: AAPG Bulletin Meeting Abstract, v.69/2, p. 246.

Courtillot, V., J. Besse, D. Vandamme, R. Montigny, J.-J. Jaeger, and H. Cappetta, 1986, Deccan flood basalts at the Cretaceous/Tertiary boundary? Earth and Planetary Science Letters v.80/3-4, p. 361-374.

Frebourg, G., S.C. Ruppel, R.G. Loucks, and J. Lambert, 2016, Depositional controls on sediment body architecture in the Eagle Ford/Boquillas system: Insights from outcrops in west Texas, United States: AAPG Bulletin, v.100/4; p. 657-682, DOI: 10.1306/12091515101

Glenister, L.M., and E.G. Kauffman, 2012, High Resolution Stratigraphy and Depositional History of the Greenhorn Regressive Hemicyclothem, Rock Canyon Anticline, Pueblo, Colorado: in Fine-Grained Deposits and Biofacies of the Cretaceous Western Interior Seaway: Evidence of Cyclic Sedimentary Processes (FG4), 1985; Copyright 2012 SEPM.

Goldman, D., S.A. Leslie, J. Nolvak, S. Young, S.M. Bergstrom, and W.D. Huff, 2007, The Global Stratotype Section and Point (GSSP) for the base of the Katian Stage of the Upper Ordovician Series at Black Knob Ridge, Southeastern Oklahoma, USA: Episodes, v. 30/4, p. 258-270.

Hamme, R.C., P.W. Webley, W.R. Crawford, F.A. Whitney, M.D. DeGrandpre, S.R. Emerson, C.C. Eriksen, K.E. Giesbrecht, J.F.R. Gower, M.T. Kavanaugh, M.A. Pena, C.L. Sabine, S.D. Batten, L.A. Coogan, D.S. Grundle, and D. Lockwood, 2010, Volcanic ash fuels anamalous plankton bloom in subarctic northeast Pacific: Geophysical Research Letters, v. 37/19, p. 1944. DOI: 10.1029/2010GL044629.

Hay, W.W., 1995, Paleoceanography of Marine Organic- Carbon–Rich Sediments: in A.Y. Huc (ed.) Paleogeography, Paleoclimate and Source Rocks, AAPG Memoir 40, p. 21.

Hill, S., 2015, Humate Controlled Ore Genesis at a Plateau-Type Uranium Deposit, Sahara Mine, Utah: AAPG Search and Discovery Article #90249; AAPG Foundation 2015 Grants-in-Aid Projects, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/abstracts/pdf/2016/90249gia/abstracts/ndx hill.pdf

Hong, H., S. Xie, and X. Lai, 2011, Volcanism in Association with the Prelude to Mass Extinction and Environment Change Across the Permian-Triassic Boundary (PTB), Southern China: GeoScienceWorld Oct. 2011; DOI: 10.1346/CCMN.2011.0590505.

Hongfu, Y., Z. Kexin, T. Jinnan, Y. Zunyi, and W. Shunbao, 2001, The Global Stratotype Section and Point (GSSP) of the Permian-Triassic Boundary: Episodes, v.24/2, p. 102-114.

Huneke, H., T. Mulder, and A.J. van Loon, 2011, Developments in Sedimentology 63, Deep-Sea Sediments: pub. Elsevier Science Dec. 22, 2011, 750 p.

Johnson, R.C., and J.E. Birdwell, 2016, Evolution of the Lower Tertiary Elko Formation, a potential lacustrine petroleum source rock in northeast Nevada: Search and Discovery Article #10966, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/documents/2017/10966birdwell/ndx birdwell.pdf

Jones, D.S., A.M. Martini, and K. Kaiho, 2016, Did Volcanism Trigger the Late Ordovician Mass Extinction? Mercury Data from South China: in GSA Abstracts with Programs. V.48/7, DOI: 10.1130/abs/2016AM-280651.

Keller, M.A., J. Macquaker, and P. Lillis, 2009, Organic Carbon-Rich Sedimentation in Early Cretaceous Arctic Sea: Nutrients Supplied by Sediment-Laden Seasonal Sea-Ice and Volcanic Ash: Search and Discovery Article #90090, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/abstracts/html/2009/annual/abstracts/keller.htm

Kumpan, T., O. Babek, J. Kalvoda, and J. Fryda, 2013, Multi-proxy stratigraphic analysis of the Devonian-Carboniferous boundary sections in Central, Western, and Southern Europe: a pathway to the better interregional correlations: In; Morocco 2013 International Field Symposium The Devonian and Lower Carboniferous of Northern Gondwana: Morocco 2013.

Li, D., 2013, Important Role of Volcanic Ashes in Forming Lacustrine Tight Oil Plays: Search and Discovery Article #90180, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/abstracts/html/2013/90180sept/abstracts/li.thm.

Lin, I.-I., C. Hu, Y-H Li, T-Y Ho, T.P. Fischer, G.T.F. Wong, J. Wu, C-W Huang, D.A. Chu, D.S. Ko, and J-P Chen, 2011, Fertilization Potential of Volcanic Dust in the Low Nutrient Low Chlorophyll Western North Pacific Subtropical Gyre {Anatahan eruption – Northern Marianas Islands} Satellite Evidence and Laboratory Study, The Global Biogeochemical Cycles First published Feb. 26, 2011, DOI: 10.1029/2009GB003758.

Marzoli, A., H. Bertrand, K.B. Knight, S. Cirilli, N. Buratti, C. Verati, S. Nomade, P.R. Renne, N. Youbi, R. Martini, K. Allenbach, R. Newerth, C. Rapaille, L. Zaninetti, and G. Bellieni, 2004, Synchrony of the Central Atlantic magmatic province and the Triassic-Jurassic boundary_climatic and biotic crisis: Geology v. 32/11; p. 973-976; DOI: 10.1130/G20652.1

Meyers, P.A., and R.M. Mitterer, 1986, Deep ocean black shales: Organic geochemistry and paleoceanographic setting. Special Issue; Marine Geology, v. 70/1-2; p.1-174.

Ormiston, A.R., and R.J. Oglesby, 1995, Effect of Late Devonian Paleoclimate on Source Rock Quality and Location: Paleogeography, Paleoclimate, and Source Rocks, Edited by Alain-Yves Huc, pub. AAPG 1995 Studies in Geology 40; DOI: 10.1306/St40595C5

Ozkan, A., C.Macaulay, D.Minisini, J.Eldrett, S.Bergman, and A.Kelly, 2014, Controls on Evolution of Pore Networks in the Eagle Ford Mudstones, South Texas, USA: Search and Discovery Article #90194, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/abstracts/html/2014/90194ice/abstracts/1947899.html

Paez-Reyes, M., A. Guerrediaga, R. Rea, J.C. Silva-Tamayo, C.K. Junium, B.V. Miller, and H. Carvajal-Ortiz, 2016, Cenomanian Volcanism and Its Influence on Carbon Cycling During Oceanic Anoxic Event 2 in the Tropical Realm: GSA Abstracts with Programs, v.48/7, DOI: 10.1130/abs/2016AM-287377

Parrish, J.T., and R.L. Curtis, 1982, Atmospheric circulation, upwelling, and organic-rich rocks in the Mesozoic and Cenozoic eras: Palaeogeography, Palaeoclimatology, Palaeoecology v.40/1-3, pp. 31-66.

Parrish, J.T., 1995, Paleogeography of Corg-Rich Rocks and Preservation Versus Production Controversy: In: Chapter 1, SG 40: Paleogeography, Paleoclimate, and Source Rocks; Edited by Alain-Yves Huc; Pub. AAPG 1995 Studies in Geology 40; DOI: 10.1306/St40595C5

Pedersen, T.F., and S.E. Calvert, 1990, Anoxia vs. Productivity: What controls the Formation of Organic-Carbon-Rich Sediments and Sedimentary Rocks? AAPG Bulletin, v.74/4, p. 454-466.

Peng, J., X Pang, X. Yang, M. Liu, H. Jiang, and S. Xiao, 2015, Genetic Relation Between Volcanic Activity and High-Quality Source Rocks of the Wenchang Formation in the Zhu 1 Depression: New Ideas on Source-Rock Evaluation in the Pearl River Mouth Basin of the South China Sea: Search and Discovery Article #90216, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/abstracts/html/2015/90216ace/abstracts/2099763.html

Richards, M.A., W. Alvarez, S. Self, L. Karlstrom, P.R. Renne, M. Manga, C.J. Sprain, J. Smit, L. Vanderkluysen, and S.A. Gibson, 2015, Triggering of the largest Deccan eruptions by the Chicxulub impact: In The GSA Field Guide 42, First published online April, 2015, DOI: 10.1130/B31167.1.

Scasso, R.A., 2001, High-Frequency Explosive Volcanic Eruptions in a Late Jurassic Volcanic Arc: The Ameghino Formation, Antarctic Peninsula:

Journal of Sedimentary Research, v.71, Jan. 2001. DOI: 10.1306/032100710101

Scudder, R.P., R.W. Murray, J.C. Schindlbeck, S. Kutterolf, F. Hauff, M.B. Underwood, S. Gwizd, R. Lauzon, and C.C. McKinley, 2016, Geochemical approaches to the quantification of dispersed volcanic ash in marine sediment: Progress in Earth and Planetary Science v.3/1; First online Jan. 4, 2015; DOI: 10.1186/s40645-015-0077-y

Sell, B., L. Ainsaar, and S. Leslie, 2013, Precise timing of the Late Ordovician (Sandbian) super-eruptions and associated environmental, biological, and climatological events: J. of the Geological Society; v.170, p. 711. First published online July 24, 2013. DOI: 10.1144/jgs2012-148.

Seubert, B.W., 2015, Volcaniclastic Petroleum Systems – Theory and Examples from Indonesia: Proceedings, Indonesian Petroleum Association, Thirty-Ninth Annual Convention & Exhibition, May 2015, paper IPA15-G-026.

Sheu, D-D., and B.J. Presley, 1986, Variations of calcium carbonate, organic carbon and iron sulfides in anoxic sediment from the Orca Basin, Gulf of Mexico: Marine Geology, v.70/1-2, p. 103-118.

Sonnenfeld, M., D. Katz, M. Odegard, C. Ohlson, and C. Zahm, 2016, Niobrara Core Poster Highlighting Bentonite Distribution and Their Impacts on Proppant Placement; Search and Discovery Article #41803, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/documents/2016/41803sonnenfeld/ndx sonnenfeld.pdf

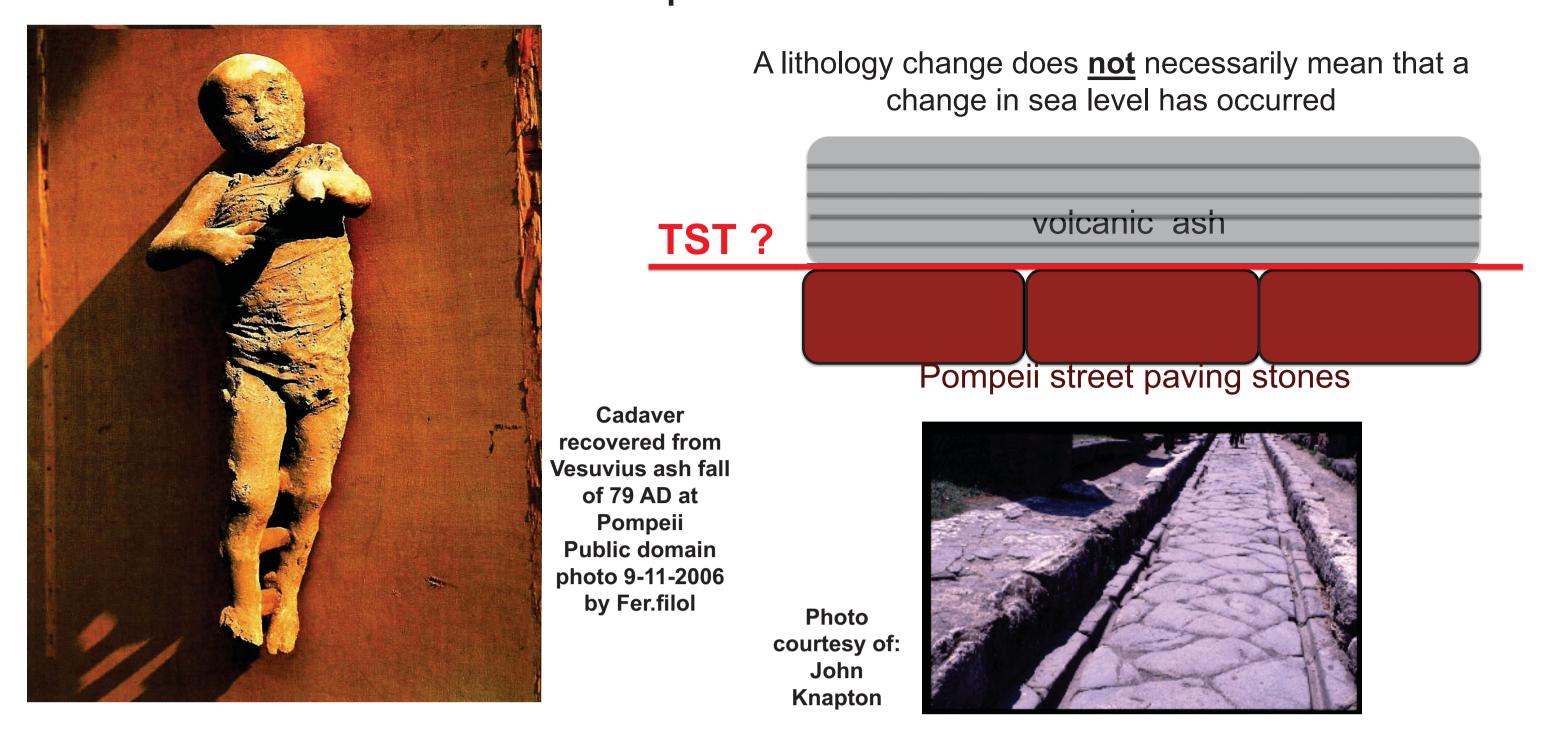
Swindles, G.T., I.T. Lawson, I.P. Savov, C.B. Connor, and G. Plunkett, 2011, A 7000 year perspective on volcanic ash clouds affecting northern Europe: Geology, v. 39/9, pp. 887-890, DOI: 10.1130/G32146.1

Wadia, A.M, 2007, Can Chemical Weathering of Volcanic Ash Result in the Formation of Chert? 2007 GSA Denver Annual Meeting Paper No. 186-12.

Wagner, T., H. Armstong, L. Heherringshaw, J. Imber, S. Floegel, and P. Hoffmann, 2015, Large Scale Climate Teleconnections Driving Marine Black Shale Formation in the Mesozoic Ocean: Conceptual Ideas from Jurassic-Cretaceous Studies: Search and Discovery Article #120178, Web Accessed September 4, 2017, http://www.searchanddiscovery.com/abstracts/pdf/2015/120178hedberg/abstracts/ndx_wagn.pdf

Williams, V. E., C.A. Ross, 1979, Depositional Setting and Coal Petrology of Tulameen Coalfield, South-Central British Columbia: AAPG Bulletin v.63/11, p. 2058-2069.

Have we sometimes misinterpreted volcanic ash in the rock record?



Millions of years later, if this cadaver was unearthed from within a thick accumulation of rocks, what description might geologists give if they found it lying on a Roman sidewalk buried in fine sediments?

This child obviously died wading in anoxic mud on the shore of an epicontinental sea at the onset of a marine transgression.

The principal assumption of sequence stratigraphy:

Through geologic time, the oceans have risen and fallen in a cyclic manner. Because of this, strata are deposited in a cyclical, predictable manner.

Is this assumption valid for the future stratigraphy of Pompeii? Is it valid for continental "cyclothems" of US continental coal deposition? Is it valid and applicable to the cyclic lithologic changes in the Eagle Ford shale?

NO TO ALL. Why? There are significant quantities of "unpredictable", altered, volcanic ash in all. Phytoplankton blooms related to ash fall are the most important reason for high organic richness of some shales and coal. Aeolian ash can cause lithological changes independent of sea level.





Volcanic ash fall -- the key to organic rich shale and coal formation

The nature of U.S. oil and gas production in recent years has prompted a more thorough examination of organic rich shales than ever before. The detailed investigation of shales has, in some cases, reached a single centimeter in vertical stratigraphic resolution in an attempt to understand the fine laminations common in many shales. The results have been surprising; and if one extends the results from the examined shales to the unexamined ones, the conclusions require a rethinking of what used to be accepted knowledge about organic rich shales and coal.

One significant contribution has come from research on the Eagle Ford Shale in South Texas. Three hundred volcanic ash layers have been identified in the Eagle Ford in the Maverick Basin (Aysen Ozkan et al., 2014), one of the "sweet spots" for oil production in the shale. The ash layers were determined to cause the organic richness of the shale by supplementing the nutrients normally limiting to oceanic primary production (Gregory Frebourg et al, 2016). Other researchers are finding similar things in other shales. Denghua Li (2013) states that "volcanic ash layers are generally observed in organic rich shales, and {the} more tuff layers {there} are, the thicker the organic-rich shale is, but volcanic ash layers are rarely found in organic fair and poor shales, and it indicates that volcanic ashes probably play an important role in forming tight oil plays." He further states that, "Volcanic ashes can stimulate plankton growth, and plankton blooms will form laminated organic-rich shales." Junwen Peng et al. (2015) concludes about the Wenchang Formation in the Pearl River Mouth Basin that, "This paper establishes the genetic relation between the high-quality source rocks, the synchronous or previous volcanic activity, and the relevant eutrophication of the water system. The volcanic activity provided the material basis for the development of high-quality source rocks." Sonnenfeld et al. (2016) have identified hundreds of ash layers in the Niobrara Shale of Colorado.

"Tonsteins (volcanic ash layers in coal – DMP) occur on almost every continent, but are best known from Europe and North America. Their geologic range is coincident with that of coal-forming environments, i.e., from Devonian to Holocene" (Bohor and Triplehorn, 1993). Sixty-five ash layers (tonsteins) have been identified in a single coal seam in Montana (Connor, 1985). B.F. Bohor and Don Triplehorn (1984) observe, "Accretionary lapilli have been identified in claystones (tonsteins) associated with coal beds of Late Cretaceous age in Wyoming, Utah, and New Mexico. The presence of accretionary lapilli in these tonstein partings confirms their volcanic origin. Similar concentric structures in other claystones not in coal, such as some flint clays, may also be accretionary lapilli, indicating a volcanic origin for these deposits." V. Eileen Williams et al. (1979) wrote about Tulameen Coalfield in British Columbia, Canada, stating that, "An abundance of tephra and bentonite indicates that volcanic activity was contemporaneous with coal and sediment deposition."

The amount of volcanic ash in a shale or coal is difficult to quantify. Volcanic glass devitrifies and the residual minerals and clays are not unique to volcanic ash and frequently are not recognized as having originated as ash. Volcanic ash mineralogy varies as does the lava and crustal material from which it comes. There is no single mineral grouping that can, in every case, define those minerals and clays in the sediment that came from ash. Once deposited, bioturbation frequently prevents the thin layers deposited from remaining distinct layers. The ash gets "dispersed" in the shales. Estimates are that much of the ash exists as dispersed ash (R.P. Scudder et al., 2016).

Is it possible that what has been discovered in the Eagle Ford Shale and in the shales of China by Denghua Li is a generalizable, nearly universal truth? Do the majority of organically rich rocks owe that richness to volcanic ash fall? Because most shales have not been examined to determine ash fall volumes, there are not many direct observations towards which to point. This author is suggesting that correlating ash fall volume in shales (and coal) with organic richness will prove enlightening.

For volcanic ash to be the primary reason for anomalous organic enrichment of rocks, some things must be true. The current explanations for enrichment must be shown to be unrealistic, and leave some characteristics of organic rich shales unexplained.

Appropriate skepticism is well expressed in the literature. The debate over whether high primary productivity, or water column anoxia, is the primary control on the formation of organic rich rocks, has produced volumes of literature. It would be impossible to give a comprehensive summary here. What follows is a necessarily selective grouping of conclusions reached by other researchers.

As true today as when it was expressed, Meyers and Mitterer (1986) state that, ".....it is clear that a satisfactory and generally accepted explanation of the paleoceanographic and depositional conditions leading to the accumulation of black shales has not yet been achieved." Wagner et al. (2014) agree; writing that, "The causal and genetic relationships controlling the timing, composition, and internal variability of these marine OC-rich shale over large distances and during variable global climate states are, still far from understood."

Meyers and Mitterer (1986) write, ".....deep water anoxic conditions are not necessarily required for deposition of sediments enriched in organic carbon." In reference to Sheu and Presley's work on the Orca Basin in the Gulf of Mexico, a modern anoxic basin, they state, "Despite the anoxic conditions, laminated sedimentary layers and enrichment in iron sulfates, the organic carbon content is only about 2%, which is less than that of most ancient laminated black shales and modern anoxic muds." Pedersen and Calvert (1990) wrote, "Sediments accumulating in the modern Black Sea, the type euxinic basin, are not particularly enriched in organic matter despite the presence of an anoxic water column....". Pedersen and Calvert (1990) conclude, "Sporadic temporal and spatial increases in primary production, reflecting changes in the behavior and/or state of the ocean-atmosphere system, constitute a more tenable explanation {than anoxic water column – DMP} for the occurrence of modern and Quaternary carbon-rich sediments and Cretaceous black shales."

The "high primary productivity" proponents (Parrish, 1995; Pederson and Calvert, 1990; others) appear to have the stronger argument. Parrish (1995) concludes that, "high biologic productivity has strongly influenced sedimentation of organic carbon." Parrish (1982) recognizes that, "upwelling zones are not necessarily highly productive, so equating upwelling with high productivity is not an ideal approach." Ormiston and Oglesby (1995) state, "Our results suggest that the primacy that has been accorded the upwelling model as a source rock predictor for at least the past decade should be abandoned." Parrish (1982) recognized that, "Although mechanisms for the genesis of anoxia have been widely discussed, mechanisms for the genesis of high biologic productivity have not; it is suggested that consideration be given to mechanisms, in addition to localized upwelling, that might promote high productivity in the oceans and the resulting high organic accumulation in the sediments."

What is missing is a mechanism that allows for the creation of high primary production, rapid burial of the algae and plankton, and the creation of an anoxic sedimentary trap for the organics so that they do not immediately decay. This paper suggests that volcanic ash fall answers those key issues as a mechanism to create organic rich rocks. If this mechanism is proven essentially accurate, a host of additional questions emerge which will subsequently have to be addressed.

The mechanism by which volcanic ash fall can produce organic rich rocks must be,

- (1) ash falls into salt water (shale) or a shallow, fresh water bog (coal), fertilizing and enhancing primary productivity (I-I Lin et al., 2010; Hamme et al., 2010),
- (2) ash sinks through the water column carrying some algae with it, and "buries alive" some algae and other phytoplankton which simultaneously sinks to the bottom,
- (3) compaction of the ash on the sea floor around the buried algae restricts the circulation of oxygenated water within the ash. The buried algae, some still alive, uses up the oxygen in its pore space and creates local anoxia. It dies but does not decay.
- (4) ash fall compaction continues, capturing the organic richness of algae and phytoplankton without the necessity of an anoxic water column or upwelling,
- (5) after some time has passed, the siliceous matrix of the ash dissolves, releasing uranium and other mobile heavy minerals into the organic rich sediments (S. Bloch et al., 1980; Scott Hill, 2015). After devitrification of the volcanic glass, the residual minerals and clays are frequently not recognized as having come from ash fall.

This mechanism changes another accepted mechanism that never quite seemed complete. The ash, after devitrification in the bottom sediments, "delivers" sometimes mobile radioactive minerals into the organic rich sediments. Radioactive minerals, rather than being concentrated in the water column by living organisms, or "scavenged from the water column by organic material", are released into the organic rich rocks once the ash is in the sediment. Release of radioactive minerals by devitrification of ash causes the high correlation between high TOC and high gamma ray log values.

The correlation between volcanism and "Oceanic Anoxic Events" with which organic rich shales are associated

There is a high correlation between the formation of black, organic rich shales and "oceanic anoxic events". The explanation that upwelling somehow becomes more significant, common, and basin-wide at these times, is difficult to believe, and cannot be directly measured. Basin-wide upwelling can only be inferred through the use of computer circulation modeling. The models are specifically designed with the results they need to achieve in mind.

Although not always believed to be the cause of the associated mass extinctions, there is also a high correlation of accelerated volcanic activity with "oceanic anoxic events". The following are some of the correlations that have been documented.

Regarding the Late Ordivician extinction event:

"Two of the largest known eruptions in the Phanerozoic produced the Ordovician Millbrig K-bentonite of North America and the Kinnekulle K-bentonite of Scandinavia......with U-Pb zircon dates of 452.86 +/- 0.29 and 454.41 +/- 0.17 Ma. These data......suggest an alternative volcanic-climate hypothesis for the Late Ordivician" (B. Sell et al., 2013).

"Our observations {Hg concentration anomalies -- DMP) are consistent with a volcanic trigger for the LOME {Late Ordovician Mass Extinction – DMP} mediated through the combined effects of glacioeustasy, changes in ocean temperature, and possible metal toxicity." (D. S. Jones et al., 2016).

Regarding the Late Devonian:

"The Viluy Traps, which cover most of the northeast margin of the Siberian Platform, have been known for four decades (Masaitis et al., 1975; Gaiduk, 1988), but only recently has their age become well constrained."

"The most recently obtained K-Ar and Ar-Ar dates indicate multiphase emplacement of the Viluy Traps between 376.7 +/- 1.7 Ma and 364.4 +/- 1.7 Ma (Ricci et al., 2013), clearly strengthening its temporal link with the Frasnian-Famennian extinction (and also implying a causal link with the lesser crisis at the Devonian – Carboniferous boundary)." "Ongoing improvements in radioisotopic dating of the Viluy Traps and Pripyat=Dnieper-Donets, as well as the marine extinction level and key developments in terrestrial ecosystems, are continuously improving the temporal link between Late Devonian volcanism and extinction(s)." (David P.G. Bond and Paul B. Wignall, 2014)

"This shift {positive peak in carbon 13 isotope value – DMP} is regarded as synchronous with the Hangenberg Black Shales, representing a horizon of enhanced organic carbon burial connected with the mass extinction event (CAPLAN & BUSTIN 1999,KAISER et al. 2006). {Devonian – Carboniferous event – DMP}. (Kumpan et al., 2013).

Regarding the Permo-Triassic "anoxic event":

"The results showed that clay minerals of the packstone bed 24e, in which the preludial mass extinction occurred at Meishan, consist of 56% mixed-layer illite-smectite (I-S), 39% illite, and 5% kaolinite. A dehydroxylation effect was measured at 652 degrees C, indicating that I-S and illite of this bed contain mainly cisvacant (cv) layers related to volcanic origin. The dehydroxylation event correlates with bed P257 at Xiakou. The white clay bed 25 also corresponding to the main extinction event at Meishan contains 95% I-S and 5% kaolinite, with a strong endothermic effect at 676 degrees C and weaker one at 514 degrees C in the DSC curve. These results are attributed to dehydroxylation of cv layers in I-S clays, suggesting that I-S in the white clay bed was derived from marine alteration of volcanic ash, in agreement with the conodont-related clay (P258) at Liakou." (Hanlie Hong et al., 2011).

"......the inception of the main stage eruption of the Tunguss Traps (Renne et al., 1995) which is regarded as synchronous with the PTB." {Permian-Triassic Boundary – DMP}.

Regarding the Triassic – Jurassic boundary event:

"The temporal relationship of the Tr-J boundary and the province's volcanism is clarified by new multi-disciplinary (stratigraphic, palynologic, geochronologic, paleomagnetic, geochemical) data that demonstrate that development of the Central Atlantic magmatic province straddled the Tr-J boundary and thus may have had a causal relationship with the climatic crisis and biotic turnover demarcating the boundary." (Andrea Marzoli et al., 2004).

Regarding the Cenomanian-Turonian {OAE-2 - the Eagle Ford time frame}:

"The coincidence of the d13C-TOC variability prior to OAE 2 and the increasing occurrence of ash layers suggests a link between volcanic activity and the carbon cycle preceding the onset of the isotopic anomaly." {see also Eagle Ford references – DMP}.

Regarding the Cretaceous – Paleogene anoxic event:

"Joint consideration of new paleomagnetic, paleontological, and geochronological data from the Deccan continental flood basalts in India and critical discussion of earlier results lead us to suggest that volcanic activity may have lasted less than 1 Ma, thus possibly ranking as one of the largest volcanic catastrophies in the last 200 Ma. Available data are best satisfied if volcanism spanned the Cretaceous/Tertiary boundary." (Vincent Courtillot et al., 1986).

"The palynomorphic Cretaceous-Tertiary boundary, based on the extinction of most species of Aquilapollenites, occurs at the base of the Ferris (No. 1) coal seam (Frenchman-Ravenscrag contact) at Ravenscrag Butte, Saskatchewan, and about one-half metre above the Nevis (No. 13) coal seam at Scollar Canyon, Alberta." (J.F. Lerbekmo, 1985).

This author believes that with improvement in the age dating of organic rich rocks, flood basalts, and explosive volcanism, the relationship between organic rich "black shales" and explosive volcanism will become more apparent. What is likely to happen, because of their relationship, is that the age dating of one will help refine the age dates of the others.

The implications of a direct relationship of volcanic ash fall to organic enrichment of shales is far reaching. As mentioned, the explanation for the correlation of TOC to high gamma ray logs would change. There are other changes which will depend on the actual volume of ash determined to be in shales.

References with underlines for emphasis by this author

If one looks for the volcanigenic contribution to organic rich rocks (and knows what to look for), one will find it.

"More than 300 interbedded volcanic ash beds are found throughout the {Eagle Ford} section in the Maverick Basin."

From: Controls on Evolution of Pore Networks in the Eagle Ford Mudstones, South Texas, USA

By: Aysen Ozkan, Calum Macaulay, Daniel Minisini, James Eldrett, Steve Bergman and Amy Kelly

In: 2014 International Conference and Exhibition, Istanbul, Turkey, September 14-17, 2014; AAPG S & Discovery Article #90194

"The Niobrara Formation has abundant very thin bentonites. All individual bentonites fall below dipole sonic and gamma ray wireline log resolution;

.....each and every one of the hundreds of thin bentonites."

From: Niobrara Core Poster Highlighting Bentonite Distribution and Their Impacts on Proppant Placement

M. Sonnenfeld, D. Katz, M. Odegard, C. Ohlson, and C. Zahm

Search and Discovery Article #41803 (2016) Posted May 16, 2016.

"Layers of altered volcanic ash and sanidine-rich crystal tuff average 1.5 cm thick and are separated by an average 7.6 cm of coal, tuffaceous coal, or carbonaceous tuff. The Big Dirty coal bed contains a rare continuous record of a period of frequent volcanic eruptions."

From: Sixty-Five Volcanic Events Recorded in Single Coal Bed: ABSTRACT

By: Carol Waite Connor

In: AAPG Bulletin; Vol. 69, Issue 2, February, 1985, p. 246

"An abundance of tephra and bentonite indicates that volcanic activity was contemporaneous with coal and sediment deposition."

From: Depositional Setting and Coal Petrology of Tulameen Coalfield, South-Central British Columbia

By: V. Eileen Williams, Charles A. Ross

AAPG Bulletin, November, 1979, Vol. 63, Issue 11, pp. 2058-2069

"Accretionary lapilli have been identified in claystones (tonsteins) associated with coal beds of Late Cretaceous age in Wyoming, Utah, and New Mexico. The presence of accretionary lapilli in these tonstein partings confirms their volcanic origin. Similar concentric structures in other claystones not in coal, such as some flint clays, may also be accretionary lapilli, indicating a volcanic origin for these deposits."

From: Accretionary Lapilli in Altered Tuffs Associated with Coal Beds

By: Bruce F. Bohor and Don M. Triplehorn

In: Journal of Sedimentary Research, Vol. 54 (1984) No. 1 (March), pp. 317-325

"Tonsteins occur on almost every continent, but are best known from Europe and North America. Their geologic range is coincident with that of coal-forming environments; i.e., from Devonian to Holocene."

From: Tonsteins: Altered Volcanic-Ash Layers in Coal-Bearing Sequences

By: Bruce F. Bohor and Don M. Triplehorn

In: Geological Society of America Special Papers 1993, v. 285, pp. 1-44; DOI: 10.1130/SPE285-p1

"Estimates are that much of the ash exists as dispersed ash."

From: Geochemical approaches to the quantification of dispersed volcanic ash in marine sediment.

By: Rachel P. Scudder, Richard W. Murray, Julie C. Schindlbeck, Steffen Kutterolf, Folkmar Hauff, Michael B. Underwood, Samantha Gwizd, Revecca Lauzon, Claire C. McKinley

In: Progress in Earth and Planetary Science Vol. 3, Issue 1, p. 1, 2016; Published by Springer Berlin Heidelberg

"The causal and generic relationships controlling the timing, composition, and internal variability of these marine OC-rich shale over large distances and during variable global climate states are, however, still far from understood."

From: Large Scale Climate Teleconnections Driving Marine Black Shale Formation in the Mesozoic Ocean: Conceptual Ideas from Jurassic-Cretaceous Studies

By: Thomas Wagner, Howard Armstrong, Liam Heherringshaw, Jonathan Imber, Sascha Floegel, and Peter Hofmann

In: AAPG Datapages/Search and Discovery Article #120178; 2015 AAPG Hedberg Research Conference, Latitudinal Controls on Stratigraphic Models and Sedimentary Concepts, September 28-October 1, 2014 – Banff, AB, Canada

Danii,

Thomas Wagner et al. 2014, refers to this Orca Basin work:

From: Variations of calcium carbonate, organic carbon and iron sulfides in anoxic sediment from the Orca Basin, Gulf of Mexico

By: Der-Duen Sheu and B.J. Presley

In: Marine Geology, Volume 70, Issues 1-2, February 1986, pp. 103-118

Other authors have concluded that there is a direct relationship between volcanic ash fall and the formation of organic rich rocks

In a discussion of the Eagle Ford/Boquillas system,

"Although it is possible that some nutrients were delivered to the basin by nonvolcanogenic processes, the co-occurrence of volcanic ash beds and globigerinid-rich sediments suggests that most nutrient input was associated with ash deposition. The cyclic alternations of globigerinid argillaceous wackestones and pelagic grainstone deposits thus appear to be primarily controlled by volcanogenic nutrient input instead of other climate or sea level—driven processes."

Depositional controls on sediment body architecture in the Eagle Ford/Boquillas system: Insights from outcrops in west Texas, United States

Gregory Frébourg, Stephen C. Ruppel, Robert G. Loucks, and Josh Lambert

AAPG Bulletin, V. 100, No. 4 (April 2016), P. 657-682.Copyright ©2016. The American Association of Petroleum Geologists. All rights reserved.DOI: 10.1306/12091515101

"Exploration cases demonstrate that organic-rich shales control tight oil plays, while cores and outcrops show that volcanic ash layers are generally observed in organic-rich shales, and more tuff layers are, the thicker the organic-rich shale is, but volcanic ash layers are rarely found in organic fair and poor shales, and it indicates that volcanic ashes probably play an important role in forming tight oil plays."

From: Important Role of Volcanic Ashes in Forming Lacustrine Tight Oil Plays

By: Denghua Li

In: AAPG datapages Search and Discovery article #90180 copyright AAPG/SEPM; China University of Petroleum/PetroChina-RIPED Joint Research Conference, Beijing, China, September 23-28, 2013

Junwen Peng et al. (2015) concludes about the Wenchang Formation in the Pearl River Mouth Basin that, "This paper establishes the genetic relation between the high-quality source rocks, the synchronous or previous volcanic activity, and the relevant eutrophication of the water system. The volcanic activity provided the material basis for the development of high-quality source rocks."

From: Genetic Relation Between Volcanic Activity and High-Quality Source Rocks of the Wenchang Formation in the Zhu 1 Depression:

New Ideas on Source-Rock Evaluation in the Pearl River Mouth Basin of the South China Sea

By: Junwen Peng, Xiongqi Pang, Xianghua Yang, Minghui Liu, Hang Jiang, and Shuang Xiao

In: AAPG Annual Convention and Exhibition abstracts, June 1, 2015, Denver CO; AAPG Search and Discovery Article #90216, May 31-June 3, 2015

"Peaks of higher organic-carbon content (up to 5.9% TOC) are associated with rare thin ash units in the pebble shale unit. In the Hue Shale, nutrient supply and organic-carbon accumulation are attributed primarily to the same processes but with relatively more influence from volcanism and less from sea-ice. Analogous Holocene processes have been shown to supply nutrients such as Fe that otherwise limit productivity at high latitudes today."

From: Organic Caron-Rich Sedimentation in Early Cretaceous Arctic Sea: Nutrients Supplied by Sediment-Laden Seasonal Sea-Ice and Volcanic Ash

By: Keller, Margaret A., Macquaker, Joe, Lillis, Paul

In: AAPG Annual Convention and Exhibition, Denver, Colorado, June 7-10, 2009; AAPG Search and Discovery Article #90090

Other authors have concluded that there is a direct relationship between volcanic ash fall and the formation of organic rich rocks

"Volcaniclastic input into stagnant oceans increases the supply and preservation of organic matter (Zimmerle, 1985; Jin et al., 1999). The contribution of volcanic material to source potential has been underrated because of: (1) a paucity of exploration in volcanic basins; and (2) the lack of volcanic components in Cretaceous and older rocks, in which the metastable minerals and vitric material has long since decomposed.

Volcanic activity contributes to organic source potential in several ways.

- The input of volcanic ash and dust into a marine basin acts as a fertilizer to promote algal bloom (Magara, 2003). The lower Eagle Ford gas shale (Texas, USA) includes tuff layers that may have enhanced organic growth (Workman, 2013; Pierce et al., 2014).
- Volcanic input into the marine environment creates ephemeral anoxic conditions that lead to the mass extinction and preservation of plankton and benthos.
- Volcanic ash decays readily to clay minerals, which can act as catalysts for transformative reactions of kerogen, the source material into hydrocarbons (Horsfield and Douglas, 1980; Jin et al., 1999)."

From: Volcaniclastic Petroleum Systems – Theory and Examples from Indonesia

By: Bernhard W. Seubert

In: Proceedings, Indonesian Petroleum Association, Thirty-Ninth Annual Convention & Exhibition, May 2015.

"Scattered air-fall tuffs indicate volcanism in northeastern Nevada during deposition of the lower part of the volcanic rich interval. Greater volcanism, indicated by thick, reworked tuffaceous intervals interspersed with volcanic rich mudrocks, appears to have occurred just prior to deposition of the richest oil shale in the Elko Formation. Large volumes of volcanic material are found in the remaining Elko lacustrine beds due to a period of prolonged volcanism in northeastern Nevada during this time."

From: Evolution of the Lower Tertiary Elko Formation, a potential lacustrine petroleum source rock in northeast Nevada

By: Ronald C. Johnson and Justin E. Birdwell

In: AAPG Pacific Section and Rocky Mountain Section Joint Meeting, Las Vegas, Nevada, October 4, 2016, Tuesday 8:55 am.

Volcanic ash fall observed to create phytoplankton blooms

".....indicating that a 2-to-5 fold increase in biological activity occurred during the week following the eruption. Satellite altimetry indicated that the bloom took place in the presence of downwelling and was not a result of upwelled nutrients in this oligotrophic ocean."

From: Fertilization Potential of Volcanic Dust in the Low Nutrient Low Chlorophyll Western North Pacific Subtropical Gyre {Anatahan eruption – Northern Marianas Islands}.

By: I-I Lin, Chuanmin Hu, Yuan-Hui Li, Tung-Yuan Ho, Tobias Fischer, George T.F. Wong, Jingfeng Wu, Chih-Wei Huang, D. Allen Chu, Dong-San Ko, and Jen-Ping Chen Revised and submitted to The Global Biogeochemical Cycles August 12, 2010.

"In August 2008, the subarctic NE Pacific experienced the largest phytoplankton bloom observed in the 12-years of chlorophyll records from SeaWIFS and MODIS ocean color satellites." "The spatial extent of the subarctic NE Pacific bloom visually matches the dispersal, and likely deposition, of volcanic ash from the 7–8 August 2008 eruption of Kasatochi volcano (52.2°N 175.5°W) in the Aleutian Islands, Alaska, USA."

From: Volcanic ash fuels anamalous plankton bloom in subarctic northeast Pacific

By: Roberta C. Hamme, Peter W. Webley, William R. Crwawford, Frank A. Whitney, Michael D. DeGrandpre, Steven R. Emerson, Charles C. Eriksen, Karina E. Giesbrecht, Jim F.R. Gower, Maria T. Kavanaugh, M. Angelica Pena, Christopher L. Sabine, Sonia D. Batten, Laurence A. Coogan, Dfamian S. Grundl, Deirdre Lockwood

In: Geophysical Research Letters, Vol. 37, Issue 19, pp. 1944-8007; First published 5 October 2010; DOI: 10.1029/2010GL044629

The concept of the formation of organic rich shales in basins with restricted/stratified circulation and an anoxic water column has been discredited. Upwelling as a mechanism is inadquate.

"Recent research suggests that high primary production and not water-column anoxia provides the first-order control on the accumulation of organic-rich facies in the modern oceans."

From: Anoxia vs. Productivity: What controls the Formation of Organic-Carbon-Rich Sediments and Sedimentary Rocks?

By: T.F. Pedersen and S.E. Calvert

In: The American Association of Petroleum Geologists Bulletin, v.74, No. 4 (April 1990), P. 454-466.

"Sediments accumulating in the modern Black Sea, the type euxinic basin, are not particularly enriched in organic matter despite the presence of an anoxic water column......"

From: Anoxia vs. Productivity: What controls the Formation of Organic-Carbon-Rich Sediments and Sedimentary Rocks?

By: T.F. Pedersen and S.E. Calvert

In: The American Association of Petroleum Geologists Bulletin, v.74, No. 4 (April 1990), P. 454-466.

"This {carbon accumulation rates} suggests that anoxic conditions in the water column may not be a prerequisite for the preservation of organic matter in marine sediments, and that models of the origin of carbonaceous facies in the geological record may therefore need to be modified."

From: Low organic carbon accumulation rates in Black Sea sediments by S.E. Calvert, R.E. Karlin, L.J. Toolin, D.J. Donahue, J.R. Southon, and J.S. Vogel From Letters to nature: Nature 350, 692-695 (25 April 1991); doi:10.1038/350692a0

In a discussion of the Cretaceous black shales of the North Atlantic,

"The abundant presence of burrowed, oxidized sediments above and below the black shales in this ocean argue against such bottom-water anoxia being extensive in either volume or duration." (Katz and Pheifer, 1982; Waples, 1983: P.A. Meyers and R.M Mitterer, 1986).

From: Introduction and Overview Special Issue Marine Geology, 70 (1986) 1-8

By: Philip A. Meyers and Richard M. Mitterer

"As discussed at length by Parrish (1982), upwelling zones are not necessarily highly productive, so equating upwelling and high productivity is not an ideal approach, but model capabilities do not permit greater sophistication at present."

From: Paleogeography of Corg-Rich Rocks and Preservation Versus Production Controversy

By: Judith Totman Parrish

In: Chapter 1, SG 40: Paleogeography, Paleoclimate, and Source Rocks; Edited by Alain-Yves Huc; Published 1995 as part of Studies in Geology 40 by AAPG

After examining the Late Cretaceous black shales around the world, "Our results suggest that the primacy that has been accorded the upwelling model as a source rock predictor for at least the past decade should be abandoned. It should be replaced by a more balanced approach to source rock prediction which would include consideration of the epeiric sea model, transgression history, and at least such climatic elements as seasonality, storm tracks, evaporation minus precipitation maps to infer location of salinity-stratified anoxia-prone basins, runoff as a source of nutrients, climatic cycles, distribution of sea surface temperature and its relation to biotic distributions or extinctions, and upwelling possibilities."

From: Effect of Late Devonian Paleoclimate on Source Rock Quality and Location

By: Allen R. Ormiston and Robert J. Oglesby

A Chapter from SG 40: Paleogeography, Paleoclimate, and Source Rocks, Edited by Alain-Yves Huc

Published 1995 as part of Studies in Geology 40; AAPG; DOI: 10.1306/St40595C5

"Although mechanisms for the genesis of anoxia have been widely discussed, mechanisms for the genesis of high biologic productivity have not; it is suggested that consideration be given to mechanisms, in addition to localized upwelling, that might promote high productivity in the oceans and the resulting high organic accumulation in sediments."

From: Paleogeography of Corg-Rich Rocks and the Preservation Versus Production Controversy

By: Judith Totman Parrish

In: AAPG Studies in Geology Vol. 40, Paleogeography, Paleoclimate, and Source Rocks, Edited by Alain-Yves Huc DOI: 10.1306/St40595C1

Supporting Information with underlines for emphasis by this author

The concept of the formation of organic rich shales in basins with restricted/stratified circulation and an anoxic water column has been discredited. Upwelling as a mechanism is inadquate.

"These results support conclusions that high biologic productivity has strongly influenced sedimentation of organic carbon. Although mechanisms for the genesis of anoxia have been widely discussed, mechanisms for the genesis of high biologic productivity have not; it is suggested that consideration be given to mechanisms, in addition to localized upwelling, that might promote high productivity in the oceans and the resulting high organic accumulation in sediments."

From: Paleogeography of Corg-Rich Rocks and Preservation Versus Production Controversy

By: Judith Totman Parrish

In: Chapter 1, SG 40: Paleogeography, Paleoclimate, and Source Rocks; Edited by Alain-Yves Huc; Published 1995 as part of Studies in Geology 40 by AAPG

"In terms of rich accumulations of marine organic matter most likely to generate petroleum, areas of ocean upwelling along continental margins are most significant." "Upwelling and nutrient availability in the upwelled waters are two different aspects of oceanographic conditions. Coastal upwelling is only one of a number of different mechanisms that bring deeper waters to the surface. High-latitude convective motions upwell and downwell large volumes of water rapidly, so that only part of the nutrients can be utilized by phytoplankton. Equatorial upwelling produces high productivity over the ocean basins but rarely impinges on continental margins. Other upwelling modes in the open ocean, such as that associated with ice margins, currents, thermo- cline domes, cyclonic eddies, and Ekman pumping, may have been significant in the past, but little is known about their geologic record. Wind-driven and Kelvin wave-driven coastal upwelling occurs on the eastern margins of the ocean basins in the tropics and subtropics, but the upwelled water is not everywhere nutrient rich. The upwelling is locally enhanced by favorable bathymetry offshore or orographic conditions on land."

> From: Paleoceanography of Marine Organic- Carbon-Rich Sediments By: William W. Hay

GEOMAR Kiel, Federal Republic of Germany and University of Colorado Boulder, Colorado, U.S.A.

".....it might be that oceanic anoxic events were in fact oceanic productivity events. Because localized upwelling is a relatively well-understood and well-modeled phenomena, little work has been done on possible mechanisms for oceanic productivity events. This would be a fruitful area of research."

From: Paleogeography of Corg-Rich Rocks and Preservation Versus Production Controversy

By: Judith Totman Parrish

In: Chapter 1, SG 40: Paleogeography, Paleoclimate, and Source Rocks; Edited by Alain-Yves Huc; Published 1995 as part of Studies in Geology 40 by AAPG

"Upwelling occurs today in about 1% of the world's oceans." (National Geographic website).

Upwelling is a local or regional phenomenon and does not explain thin organic rich beds deposited across the majority of any ocean basin. Upwelling would produce thick organic rich sediments in the area of the upwelling. Thick local or regional accumulations of organic rich strata conflict with the interpretation that these strata are part of a transgressive systems tract and therefore a condensed section. (This author)

Volcanic Ash as a Uranium Source

In discussing the mechanism for Uranium deposition in the Morrison Formation:

"Swamps that developed along braided stream systems in the Salt Wash experienced abundant volcanic ash-fall deposition during the late Jurassic. Humic-acid within these swamps leached uranium and other metals from ash. This reducing source fluid fell into surrounding channel sandstone "sieves" under gravity or during compaction of the swamp shales."

From: Humate Controlled Ore Genesis at a Plateau-Type Uranium Deposit, Sahara Mine, Utah

By: Scott Hill

In: AAPG Search and Discovery Article #90249 Copyright AAPG Foundation 2015 Grants-in-Aid Projects

"Chemical changes during its devitrification are characterized by a loss of silicon, sodium, potassium, and uranium, and addition of magnesium to the ash. The thorium to uranium ratios range from 4:1 to 10:1 for relatively unaltered ash to 16:1 to 64:1 for the highly altered ash."

"Analyses of the Pearlette ash {relatively unaltered ash - DMP} did not disclose any alteration trends or a downward decrease in the uranium concentration. The uranium content of the Pearlette is significantly higher than that of the altered Ogallala ash. The minimum age of the Pearlette is 0.6 m.y. which suggests that efficient release of uranium from volcanic glass, at least in some examples, is not a geologically contemporaneous process."

From: Distribution and Alteration of Ogallala Volcanic Ash Deposits and Their Possible Relation to Uranium Mineralization in Western Oklahoma: ABSTRACT

By: S. Bloch, Kenneth S. Johnson

In: AAPG Bulletin, Vol. 64 (1980), Issue 5 (May); pp. 677-678.

"An extrapolation over the life-time of major Pacific volcanic arcs and hotspot chains, combined with a volume estimate of the distal tephra component, indicates...........23% (by volume) of the Pacific oceanic sediments {are volcanogenic -- DMP}."

From: Developments in Sedimentology 63; Deep-Sea Sediments Edited By: H. Huneke and T. Mulder; Series Editor: A.J. van Loon Published by: Elsevier B.V., 2011

Dispersed ash within a sequence by Scudder

"....the presence/absence of very fine-grained ash material, and identification of its composition in particular, is challenging given its broad classification as an "aluminosilicate" component in sediment. Given this challenge, many studies of ash have focused on discrete layers (that is, layers of ash that are of millimeter-to-centimeter or greater thickness, and their respective glass shards) found in sequences at a variety of locations and timescales and how to link their presence with a number of Earth processes. The ash that has been mixed into the bulk sediment, known as dispersed ash, has been relatively unstudied, yet represents a large fraction of the total ash in a given sequence."

From: Geochemical approaches to the quantification of dispersed volcanic ash in marine sediment

First Online: 04 January 2016

DOI: 10.1186/s40645-015-0077-y

Scudder, R.P., Murray, R.W., Schindlbeck, J.C. et al. Prog. in Earth and Planet. Sci. (2016) 3: 1. doi:10.1186/s40645-015-0077-y

Chert from volcanic ash

"The evidences gathered from all of the above mentioned methods indicated chemical weathering to be responsible for the formation of chert in the volcanic ash horizon of the Reid's Mistake Formation."

> From: Can Chemical Weathering of Volcanic Ash Result in the Formation of Chert? By: Wadia, Adil Minoo

In: 2007 GSA Denver Annual Meeting (28-31 October, 2007) Paper No. 186-12

This author is suggesting a causal mechanism for organic rich shales and coals, not extinctions.

There is no scientific consensus on the cause(s) for the earth's major extinctions.

The association of organic rich shales with OAE's means volcanism must also be associated with the extinction events. There has been major volcanism associated with each; sometimes, but not always, invoked as a cause.

Regarding the Late Ordovician anoxic event:

"Two of the largest known eruptions in the Phanerozoic produced the Ordovician Millbrig K-bentonite of North America and the Kinnekulle K-bentonite of Scandinavia, which have been previously suggested to be coeval. The Millbrig K-bentonite from Kentucky, USA and the Kinnekulle K-bentonite from Bornholm, Denmark yielded chemical abrasion thermal ionization mass spectrometry U–Pb zircon dates of 452.86 ± 0.29 and 454.41 ± 0.17 Ma (2σ analytical uncertainty), respectively, thus showing significant age differences contrary to what is generally held. These data and four additional newly dated K-bentonites directly establish the first radioisotopic age constraints for the Ordovician Katian–Sandbian global stage boundary, refine global stratigraphic correlations, date associated chemostratigraphic events, and suggest an alternative volcanic–climate hypothesis for the Late Ordovician"

From: Precise timing of the Late Ordovician (Sandbian) super-eruptions and associated environmental, biological, and climatological events

By: B. Sell, L. Ainsaar, and S. Leslie

In: Journal of the Geological Society; 170, pp. 711-714; First Published online July 24, 2013. DOI: 10.1144/jgs2012-148

We suggest the elevated Hg loading may be the product of a substantial and prolonged volcanic eruption. We propose that sulfur aerosols emitted during the eruption disturbed the planet's radiative balance and allowed for the expansion of Gondwanan ice sheets and sea level fall; cessation of volcanism allowed radiative balance and ice volume to relax to a state similar to that prior to the excursion. While elevated Hg concentrations have been linked to eruption of large igneous provinces coincident with other Phanerozoic mass extinctions, the climate response during the LOME {Late Ordovician Mass Extinction – DMP} may have been unique owing to different geological boundary conditions and the rates and magnitudes of volcanic forcing. Our observations are consistent with a volcanic trigger for the LOME mediated through the combined effects of glacioeustasy, changes in ocean temperature, and possibly metal toxicity.

From: Did Volcanism Trigger the Late Ordovician Mass Extinction? Mercury Data from South China

By: Jones, David S., Martini, Anna M., and Kaiho, Kunio

In: Geological Society of America Abstracts with Programs. Vol. 48, No. 7, DOI: 10.1130/abs/2016AM-280651

"The Global Boundary Stratotype Section and Point (GSSP) for the Katian Stage of the Upper Ordovician Series is defined as the 4.0 m-level above the base of the Bigfork Chert in the Black Knob Ridge section, south- eastern Oklahoma."

"This stratigraphic level is also in close proximity to several important marker horizons - just above the Millbrig and Kinnekulle K-bentonite com- plexes in eastern North America and Scandinavia, respectively, and just below the beginning of the Upper Ordovician Guttenberg (GICE) !13C excursion."

"At the BKR section, approximately 50 meters of black, graptolite-rich Womble Shale are exposed (Figure 4). The upper Womble Shale is composed of soft, tan to chocolate brown-weathering shale and bedded chert. In addition to graptolites, these beds contain conodonts, chitinozoans, sponge spicules, inarticulate brachiopods, and well-rounded quartz sand grains. Conformably overlying the Womble Shale are approximately 145 meters of Bigfork Chert (Figures 4 and 5). The contact between the two units appears gradational. The base of the Bigfork Chert is a 0.5 meter interval of hard, splintery black shale that contains abundant conodonts and chitinozoans. The Bigfork Chert is composed of nodular and bedded chert, which is intercalated with black shale and siliceous limestone. Limestone beds are absent in the shale above the Bigfork Chert, and the upper boundary of the Big- fork Chert is placed at the last limestone bed in the section (Finney, 1988)."

From: The Global Stratotype Section and Point (GSSP) for the base of the Katian Stage of the Upper Ordovician Series at Black Knob Ridge, Southeastern Oklahoma, USA

By: Goldman, Daniel; Leslie, Stephen A.; Nolvak, Jaak; Young, Seth; Bergstrom, Stig M.; and Huff, Warren D.

In: Episodes 30/4, pp. 258-270

Regarding the Late Devonian:

"The Viluy Traps, which cover most of the northeast margin of the Siberian Platform, have been known for four decades (Masaitis et al., 1975; Gaiduk, 1988), but only recently has their age become well constrained."

"The most recently obtained K-Ar and Ar-Ar dates indicate multiphase emplacement of the Viluy Traps between 376.7 +/- 1.7 Ma and 364.4 +/- 1.7 Ma (Ricci et al., 2013), clearly strengthening its temporal link with the Frasnian-Famennian extinction (and also implying a causal link with the lesser crisis at the Devonian – Carboniferous boundary)." "Ongoing improvements in radioisotopic dating of the Viluy Traps and Pripyat=Dnieper-Donets, as wee as the marine extinction level and key developments in terrestrial ecosystems, are continuously improving the temporal link between Late Devonian volcanism and extinction(s)."

From: Large igneous provinces and mass extinctions: An update By: David P.G. Bond and Paul B. Wignall

In: The Geological Society of America Special Paper 505, Volcanism, Impacts, and Mass Extinctions: Causes and Effects; Edited by Gerta Keller and Andrew C. Kerr, 2014, p. 36

"This shift {positive peak in carbon 13 isotope value – DMP} is regarded as synchronous with the Hangenberg Black Shales, representing a horizon of enhanced organic carbon burial connected with the mass extinction event (CAPLAN & BUSTIN 1999,KAISER et al. 2006). {Devonian – Carboniferous event – DMP}.

From: Multi-proxy stratigraphic analysis of the Devonian-Carboniferous boundary sections in Central, Western, and Southern Europe: a pathway to the better interregional correlations.

By: Kumpan, T, Babek, O., Kalvoda, J., Fryda, J.

In: Morocco 2013 International Field Symposium "The Devonian and Lower Carboniferous of northern Gondwana."

Regarding the Permo-Triassic "anoxic event":

"The results showed that clay minerals of the packstone bed 24e, in which the preludial mass extinction occurred at Meishan, consist of 56% mixed-layer illite-smectite (I-S), 39% illite, and 5% kaolinite. A dehydroxylation effect was measured at 652°C, indicating that I-S and illite of this bed contain mainly cis-vacant (cv) layers related to volcanic origin. The dehydroxylation event correlates with bed P257 at Xiakou. The white clay bed 25 also corresponding to the main extinction event at Meishan contains 95% I-S and 5% kaolinite, with a strong endothermic effect at 676°C and a weaker one at 514°C in the DSC curve. These results are attributed to dehydroxylation of cv layers in I-S clays, suggesting that I-S in the white clay bed was derived from marine alteration of volcanic ash, in agreement with the conodont-correlated clay (P258) at Xiakou."

From: Volcanism in Association with the Prelude to Mass Extinction and Environment Change Across the Permian-Triassic Boundary (PTB), Southern China

By: Hanlie Hong, Shucheng Xie, and Xulong Lai

In: GeoScienceWorld; DOI: 10.1346/CCMN.2011.0590505 Published on October 2011

"Bed 25 is a white ash clay 13 cm below PTB, which gives an average age (by four author groups) of 251.23 Ma. Bed 28 is an ash clay 8 cm above PTB, which gives an average age (by two author groups) of 251.2 Ma. It may be relatively safe to set the PTB age briefly at 251 Ma. Mundil et al. (2001) declared a U/Pb single-crystal age of ~253 Ma for the PTB in Meishan. This however is remarkably older than both the above estimation and the 250.0 ± 0.3 Ma age (40Ar/39Ar) of the inception of main stage eruption of the Tunguss Traps (Renne et al., 1995), which is regarded as synchronous with the PTB. As there is as yet no notable radiometric dating in other parts of the world, pending further re-investigation we temporarily use 251 Ma for the age of PTB."

From: The Global Stratotype Section and Point (GSSP) of the Permian-Triassic Boundary By: Yin Hongfu, Zhang Kexin, Tong Jinnan, Yang Zunyi, and Wu Shunbao In: Episodes, Vol. 24, No. 2

Regarding the Triassic – Jurassic boundary:

"The temporal relationship of the <u>Tr-J boundary</u> and the province's volcanism is clarified by new multi-disciplinary (stratigraphic, palynologic, geochronologic, paleomagnetic, geochemical) data that demonstrate that development of the Central Atlantic magmatic province straddled the Tr-J boundary and thus may have had a causal relationship with the climatic crisis and biotic turnover demarcating the boundary."

From: Synchrony of the Central Atlantic magmatic province and the <u>Triassic-Jurassic boundary</u> climatic and biotic crisis

By: Marzoli, Andrea; Bertrand, Herve; Knight, Kim B.; Cirilli, Simonetta; Verati, Chrystele; Nomade, Sebastien; Renne, Paul R.; Youbi, Nasrrddine; Martini, Rossana; Allenbach, Karin; Neuwerth, Ralph; Rapaille, Cedric; Zaninetti, Louisette; Bellieni, Giuliano

In: 2004 Geological Society of America; Geology: November, 2004; v. 32, No. 11; pp. 973-976; DOI: 10.1130/G20652.1

"Two <u>Cenomanian-Turonian</u> {OAE-2 – DMP} organic-rich mudstone successions from the Upper Magdalena Valley, Colombia display d¹³C_{TOC} variability that is typical of OAE 2, in addition to the precursor events. Thin ash beds are commonly found (ca. 60 beds) and provide clues to the coupling between carbon cycling and regional volcanism. The coincidence of the d¹³C_{TOC} variability prior to OAE 2 and the increasing occurrence of ash layers suggests a link between volcanic activity and the carbon cycle preceding the onset of the isotopic anomaly."

From: Cenomanian Volcanism and Its Influence on Carbon Cycling During Oceanic Anoxic Event 2 in the Tropical Realm
By: Paez-Reyes, Manuel; Guerrediaga, Ashley; Rea, Rebecca; Silva-Tamayo, Juan Carlos; Junium, Christopher K.; Miller, Brent V.; and Carvajal-Ortiz, Humberto
In: Geological Society of America Abstracts with Programs, Vol. 48, No. 7; DOI: 10.1130/abs/2016AM-287377

Regarding the Hesseltal Formation near Wunstorf, Germany, deposited from Late Cenomanian through Early Turonian:

"Biogeochemical data of a sedimentary succession of BS {Black Shale – DMP} and calcareous nannofossil ooze deposited in a shelf setting of the OAE 2 suggest that BS formation was induced by enhanced inputs of imbalanced nutrients due to high weathering rates and continental run-off triggered by a pCO2, resulting from the CLIP {Caribbean Large Igneous Province – DMP} eruptions."

From: Imbalanced nutrients as triggers for black shale formation in a shallow shelf setting during the OAE 2 (Wunstorf, Germany)

By: M. Blumenberg and F. Wiese

In: Biogeosciences, 9, pp. 4139-4153, 2012: DOI: 10.5194/bg-9-4139-2012.

"Joint consideration of new paleomagnetic, paleontological and geochronological data from the Deccan continental flood basalts in India and critical discussion of earlier results lead us to suggest that volcanic activity may have lasted less than 1 Ma, thus possibly ranking as one of the largest volcanic catastrophes in the last 200 Ma. <u>Available data are best satisfied if volcanism spanned the Cretaceous/Tertiary boundary</u>."

From: Deccan flood basalts at the Cretaceous/Tertiary boundary?

By: Vincent Courtillot, Jean Besse, Didier Vandamme, Ramond Montigny, Jean-Jacques Jaeger, Henri Cappetta
In: Earth and Planetary Science Letters; Vol. 80, Issues 3-4, November 1986, pp. 361-374.

Evidence that widespread volcanism occurred at OAE2 from Colorado to Texas (Eagle Ford) implying that even at well-studied outcrops, researchers may be underestimating the significance of ash fall to cyclical sedimentation and organic richness in the Cretaceous western interior seaway

"The Greenhorn cyclothem has become the model for eustatically-generated, third-order, cyclic sedimentation in Cretaceous epicontinental settings. The Rock Canyon Anticline sequence near Pueblo, Colorado, is the standard reference section for this cyclothem. The Greenhorn transgressive hemicyclothem (including the Muddy Sandstone, Mowry Shale, Graneros Shale, and the Greenhorn Formation through the middle Bridge Creek Limestone Member) has been the subject of detailed stratigraphic and paleontological study for many years."

"...the regressive sequence of the Greenhorn Cyclothem is coarser-grained, more bioturbated, less laminated, and contains lower percentages of organic carbon than equivalent transgressive facies. Greater current circulation and higher levels of benthic oxygenation are implied during regression. Volcanic ash (bentonite) beds are extremely common in transgressive facies, and comparatively rare in regressive facies; this suggets a major slowdown in tectonism and associated volcanism during eustatic fall and regional regression."

From: High Resolution Stratigraphy and Depositional History of the Greenhorn Regressive Hemicyclothem, Rock Canyon Anticline, Pueblo, Colorado

By: Linda M Glenister and Erle G. Kauffman

In: Fine-Grained Deposits and Biofacies of the Cretaceous Western Interior Seaway: Evidence of Cyclic Sedimentary Processes (FG4), 1985; Copyright 2012 SEPM

NOTE: See also the Eagle Ford shale references

Walter Alvarez (author T. Rex and the Crater of Doom) authors paper on impact triggering volcanism

"It is therefore reasonable to hypothesize that the Chicxulub impact might have triggered the enormous Poladpur, Ambenali, and Mahabaleshwar (Wai Subgroup) lava flows, which together may account for >70% of the Deccan Traps main-stage eruptions. This hypothesis is consistent with independent stratigraphic, geochronologic, geochemical, and tectonic constraints, which combine to indicate that at approximately Chicxulub/Cretaceous-Paleogene time, a huge pulse of mantle plume-derived magma passed through the crust with little interaction and erupted to form the most extensive and voluminous lava flows known on Earth."

From: Triggering of the largest Deccan eruptions by the Chicxulub impact

By: Mark A. Richards, Walter Alvarez, Stephen Self, Leif Karlstrom, Paul R. Renne, Michael Manga, Courtney J. Sprain, Jan Smit, Loyc Vanderkluysen, and Sally A. Gibson In: The Geological Society of America Field Guide 42, First published online April, 2015, DOI: 10.1130/831167.1

Estimates of Frequency of Explosive Volcanic Eruptions

From tree-ring density data northern hemisphere (K.R.Briffa et al., 2015)

9 climate-altering eruptions in 600 years (1400 to 2000; 1453, 1601, 1641/42, 1666, 1695, 1698, 1816, 1884, 1912)

In the 9,700,000 years to deposit Eagle Ford: (9,700,000/600 = 16,167 X 9 = 145,503 eruptions worldwide during Eagle Ford Deposition at rate of last 600 years

In the 25,000,000 years to deposit Barnett Shale: (25,000,000/600 = 41,667 X 9 = 375,003 eruptions worldwide in time of deposition of Barnett Shale

From High-Frequency Explosive Eruptions in a Late Jurassic Volcanic Arc: The Ameghino Formation, Antarctic Peninsula (Roberto A. Scasso, 2001)

Average interval between Late Jurassic explosive eruptions 700 – 1000 years (similar to rates in currently active volcanic arcs - Scasso)

In the 9,700,000 years to deposit the Eagle Ford: (9,700,000/1000 = **9700** eruptions from a single island arc during Eagle Ford deposition

In the 25,000,000 years to deposit the Barnett Shale: (25,000,000/1000 = **25,000** eruptions from a single island arc during Barnett Shale deposition

From ash fall deposits in European peats; ash falls for the most recent 1000 years occurred on average 56 +/- 9 years (65 years used in calculation -- Graeme T. Swindles, et al., 2011)

In the 9,700,000 years to deposit the Eagle Ford (9,700,000/65 = **149,231** eruptions from Icelandic complex alone

In the 25,000,000 years to deposit the Barnett Shale (25,000,000/65 = **384,615** eruptions from Icelandic complex alone