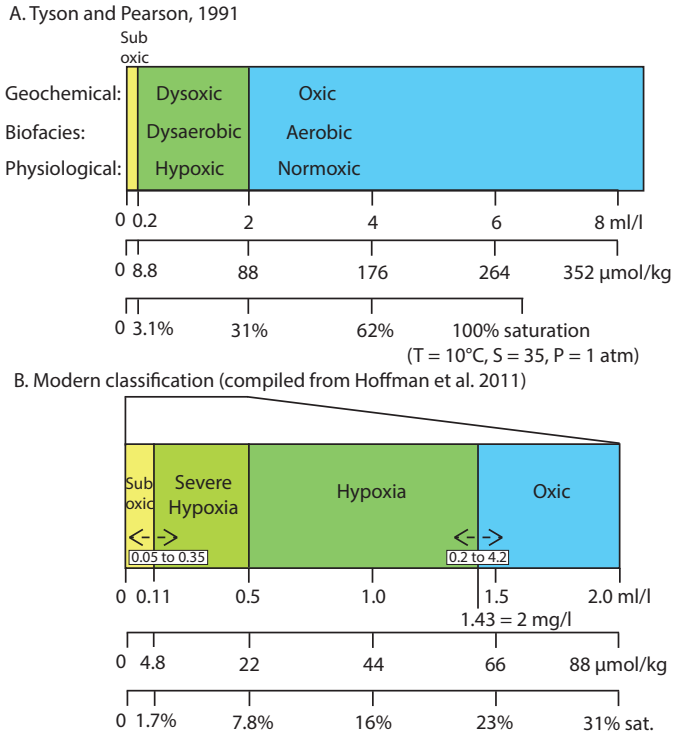
SPODDS
Stanford Project On Deepwater Depositional Systems

SPODDS 27th ANNUAL REVIEW AND FIELD WORKSHOP

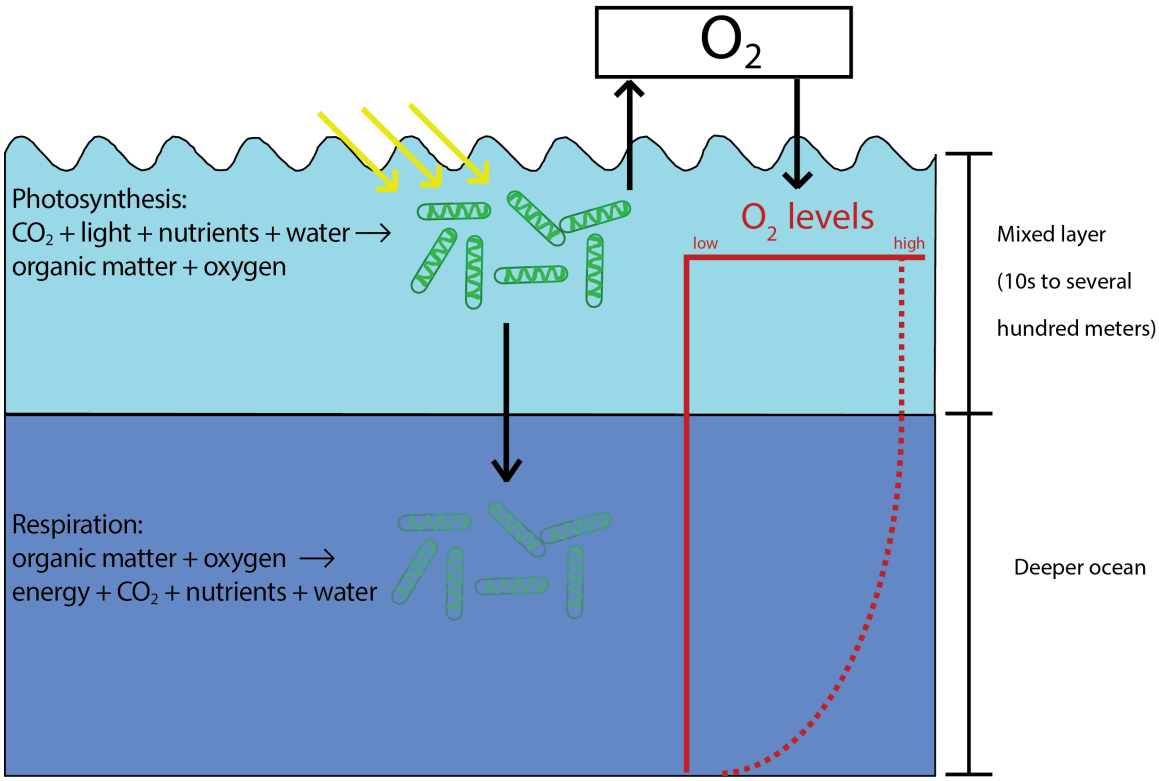
Shale Geochemistry Short Course Take-home messages

Development of anoxic conditions

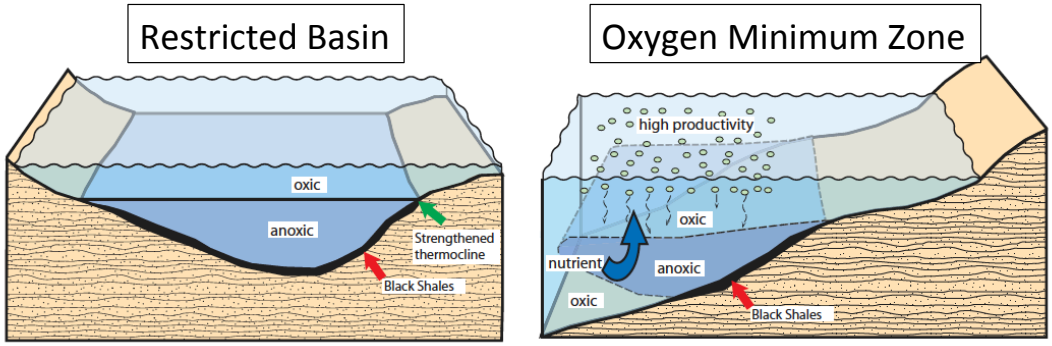


Nomenclature of low-oxygen conditions. Older terminology above from Tyson and Pearson, 1991. Modern classification below compiled from Hoffman et al., 2011 by Sperling et al., 2015, Annual Reviews. Geochemists also define two flavors of anoxia (zero oxygen):

Ferruginous- No oxygen and free ferrous iron (Fe^{2+}), no sulfide
Euxinic- No oxygen and free sulfide



Low-oxygen/anoxic conditions and high organic carbon black 'shales' can develop in a number of different ways in different oceanographic settings. This includes the amount of oxygen in the atmosphere, the amount of oxygen in equilibrium with the water column (controlled by temperature/salinity), the mixing of the local water column (stratification) and the water-mass residence time, and the nutrient inputs that fuel phytoplankton production. These phytoplankton then sink below the mixed layer, and are respired/remineralized, drawing down oxygen in the water column.



- Restricted systems (mid-continent late Paleozoic shales)
  -Anoxia can be sustained with relatively normal OC production
  -Anoxia due to restriction and long residence times
  -Anoxia may fluctuate but may also be stable (e.g. Black Sea)

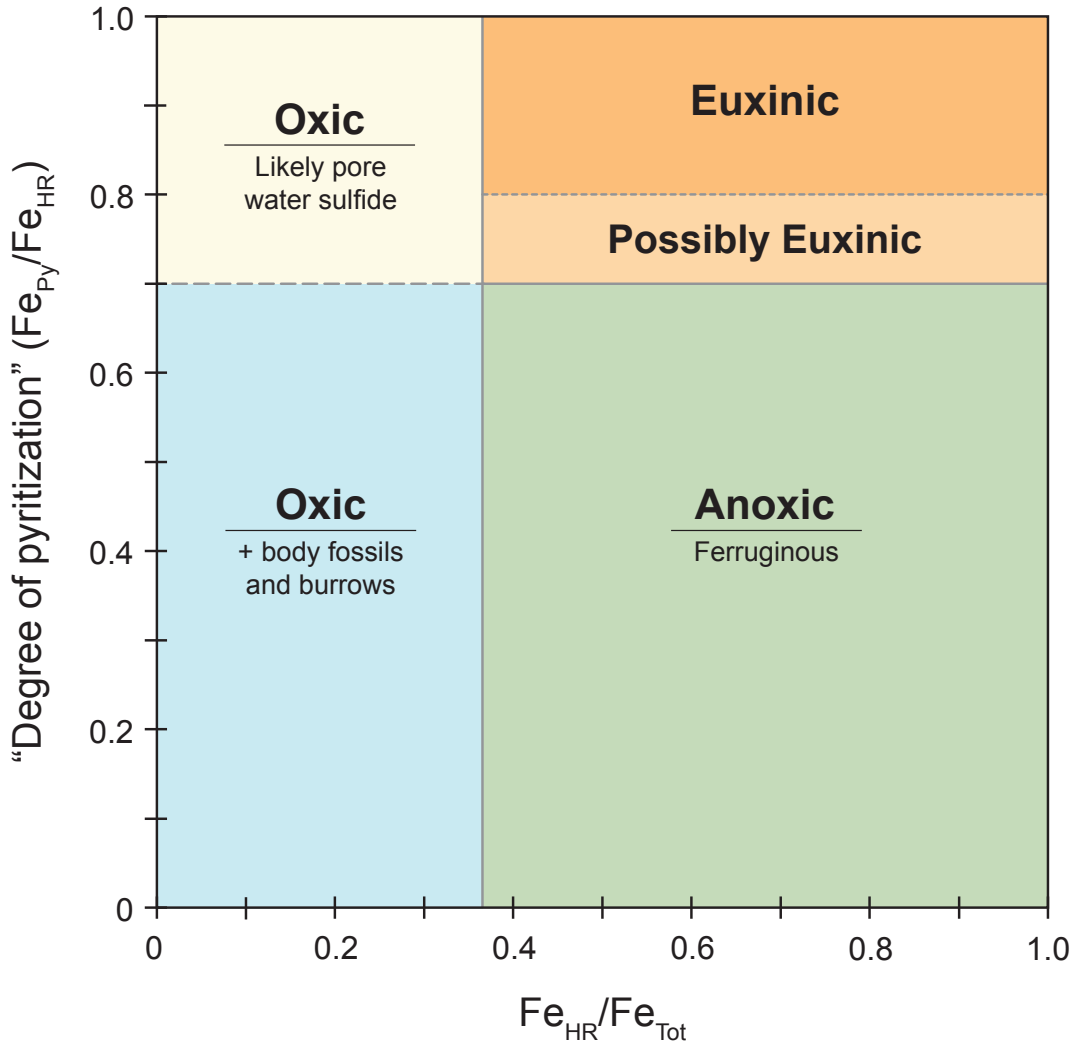
- Upwelling systems (Monterey Formation, Shublik Formation)
  -Relatively high organic carbon production/delivery
  -High remineralization rates
  -Anoxia perhaps relatively rare/ episodic due to short water-residence times
  -Anoxia often ferruginous rather than euxinic

In an end-member sense, most black shales are deposited in either restricted basins or Oxygen Minimum Zone settings. In restricted basins, low oxygen conditions develop because of the long time period for which the water mass is out of contact with the atmosphere—given enough time, even a very low rate of organic carbon delivery to the isolated water mass will result in aerobic respiration, oxygen drawdown, and anoxia. In Oxygen Minimum Zones (OMZs), water mass residence times are short, but there is so much organic carbon being put into the system that the oxygen is depleted. There are hybrid depositional environments, for instance the California Borderland Basins are both restricted basins with a tectonic sill and are also intersected by the Oxygen Minimum Zone.

Iron geochemistry

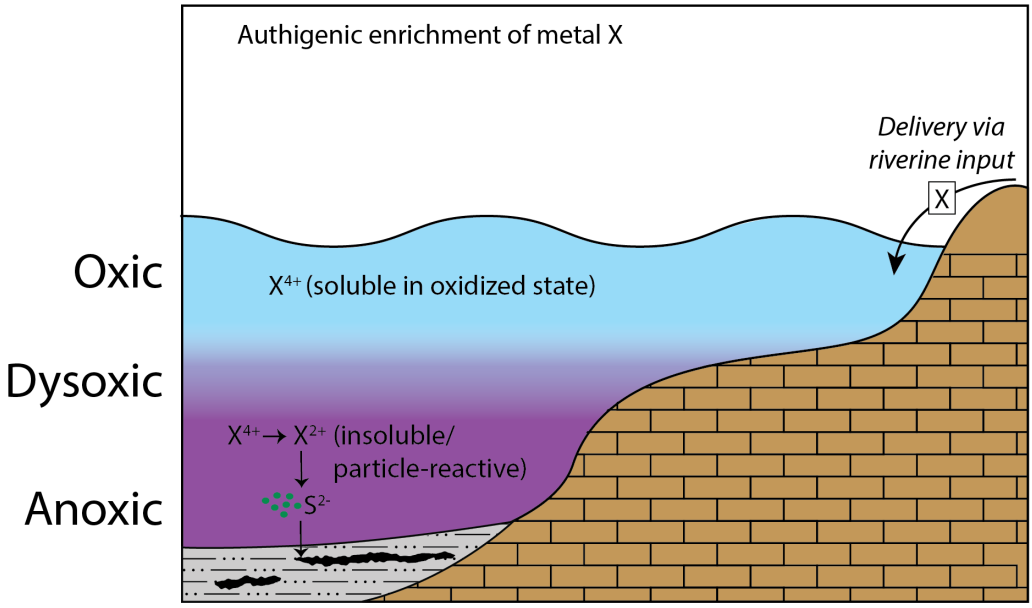
- ***Fe-pyrite (FeP):*** Iron in the form of pyrite
  -Operational definition: Calculated stoichiometrically (assuming FeS_2) from sulfide released during CRS extraction
- ***Fe-carbonate:*** Iron contained in carbonates such as siderite and ankerite. Extractable with sodium acetate (soft acid digestion)
- ***Fe-oxide (FeD):*** Iron oxides such as hematite and goethite. Extractable with sodium dithionite.
- ***Fe-magnetite:*** Iron in magnetite. Extractable with ammonium oxalate

- ***Highly reactive iron (FeHR):*** Iron in pyrite plus iron that is reactive to sulfide on early diagenetic timescales**.** Sum of FeP + iron extractable in acetate, dithionite and oxalate extractions. The definition is important: it allows some relationships to be self-evident based on the definition (specifically euxinia)
- ***Euxinic:*** anoxic water column with free sulfide
- ***Ferruginous:*** anoxic water column with free ferrous iron



Interpretive framework for iron speciation data. **Iron speciation is the only proxy that can reliably identify ferruginous versus euxinic conditions.** Because rapid sedimentation does not allow sufficient time for authigenic enrichments in the sediment, sediments deposited rapidly under an anoxic water column will have a false 'oxic' signature. Consequently, some workers recognize an 'equivocal' zone at ~0.2-0.22 (Sperling et al., 2016, Geological Society of America Bulletin). Figure made by SPODDS doctoral student Sam Ritzer.

Redox Sensitive Trace Metals

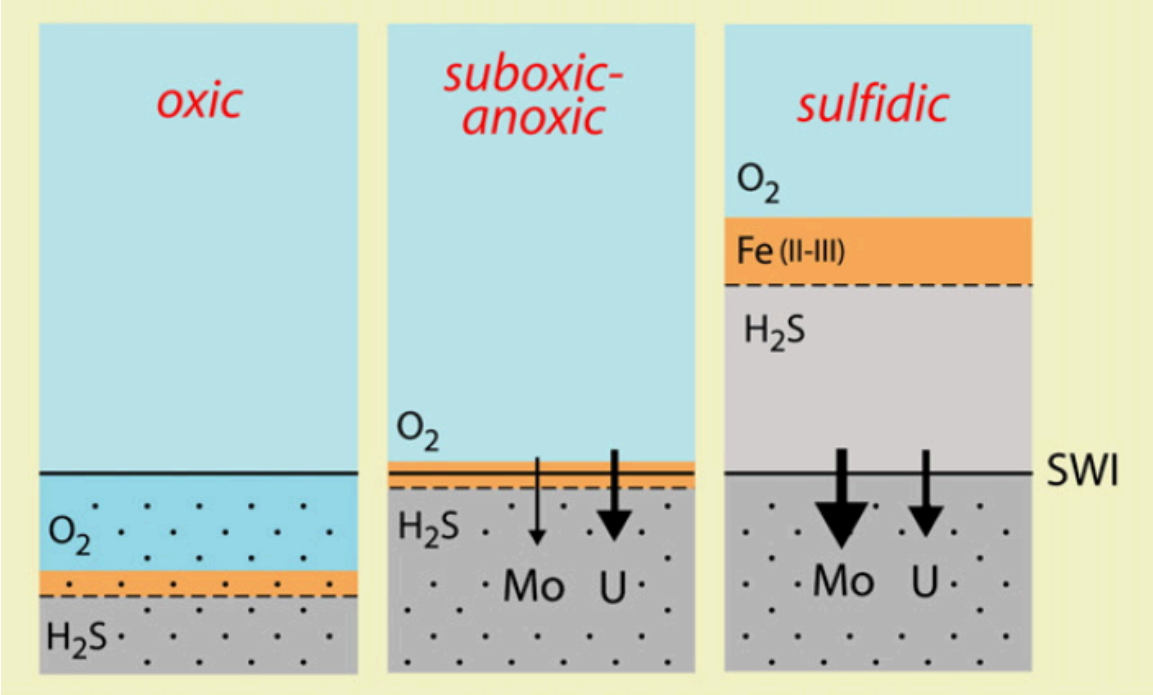


Authigenic enrichment of a hypothetical redox-sensitive trace metal (X). Metal X is delivered to the ocean through both dissolved and detrital riverine input. The dissolved metals remain soluble when they are in oxygenated seawater. In more reducing (anoxic) seawater, the metal is reduced and becomes insoluble (reacts with particles in seawater such as organic matter or sulfides) to become sequestered in the sediment. If these authigenic metal enrichments are much higher than the background detrital input, one can assume a reducing water column. The exact reduction conditions and metal host will vary between metals.

Table 1
Characteristics of molybdenum and uranium.

Characteristic	Molybdenum	Uranium
Biologically essential element	Yes	No
Ocean distribution	Conservative	Conservative; a small but variable fraction of is associated with particulate organic carbon
Salinity-normalized dissolved concentration	110 nM	13 nM
Modern-ocean residence time	0.78 million years	0.45 million years
Main source of metal	Rivers	Rivers
Main species in oxic sea water and oxidation state	MoO_4^{2-}/Mo(VI)	$UO_2(CO_3)_3^{4-}$/(U(VI))
Speciation in reducing conditions	Thiomolybdates $MoO_xS_{4-x}^{2-}$	UO_2, U_3O_7 or U_3O_8
Main mechanisms of transfer to sediments	In oxic settings, Mo scavenging by metal oxides, notably Mn (probable speciation change from the dissolved MoO_4^{2-} to the particle reactive MoO_3). In reducing settings with free HS^-, Mo is converted to particle reactive thiomolybdates that are scavenged from solution *via* sulfidized (organic S-rich) organic material r *via* Mo capture by Fe–S phases. At low [HS^-], Mo uptake probably occurs in the presence of Fe, possibly mediated by a Fe—S phase. At high sulfide concentrations, uptake must operate in the absence of dissolved iron possibly mediated by a metal sulfide such as MoS_4^{2-}.	The main removal mechanism operates via uptake across the sediment-water interface of reducing sediments. Under conditions close to the Fe(III)–Fe(II) transition, soluble U (VI) is reduced to insoluble U(IV), the uptake of which may be accelerated by the formation of organometallic ligands and the influence of organic substrates in the sediment. The accumulation is at least partly mediated by bacterial sulfate reduction reactions, because without bacterial activity, the reduction process is slow. As sulfate reduction intensity is linked to reactive organic matter abundance, U concentration is usually correlated with the organic carbon rain rate and content in anoxic (non-sulfidic) facies.

'Cheat sheet' for molybdenum and uranium, two of the most commonly measured and best understood redox-sensitive trace metals.



Comparison of Mo and U behavior. Lack of redox-sensitive trace metal enrichments indicates an oxic water column (note though that muted enrichments under ferruginous conditions can be very difficult to detect—it is far easier to demonstrate the presence of an enrichment than the lack of one). Enrichments in U but not Mo can demonstrate a suboxic or ferruginous (anoxic but non-sulfidic) water column, and large enrichments in Mo fingerprint a euxinic water column. Figure from Algeo and Tribovillard, 2009.

Three levers on Mo enrichments

- Local redox state
  -No sulfide, No Mo
- Total organic carbon contents
  -Mo is hosted in TOC
  -Increased production drives euxinia
- Aqueous (dissolved) Mo concentration
  -Global redox landscape
  -Basin restriction

Controls on enrichment level of molybdenum. The most important control is the local redox state—if sulfide is not present, enrichments will be absent or very low. The next control is the level of organic carbon, in part because Mo is binding to organic carbon, and in part because the development of euxinia is often driven by organic carbon loading/high primary productivity. The final control is the dissolved Mo concentration in the water column. During times of expanded global euxinia (e.g., OAEs) or in a highly

restricted basin (like the modern Black Sea), the dissolved seawater concentration will be low. Authigenic Mo enrichments will then be quite low in spite of euxinic conditions.

These general controls also apply to other redox-sensitive trace metals but with differences based on their individual behavior (what conditions they are reduced at, specific host in sediments, etc.).

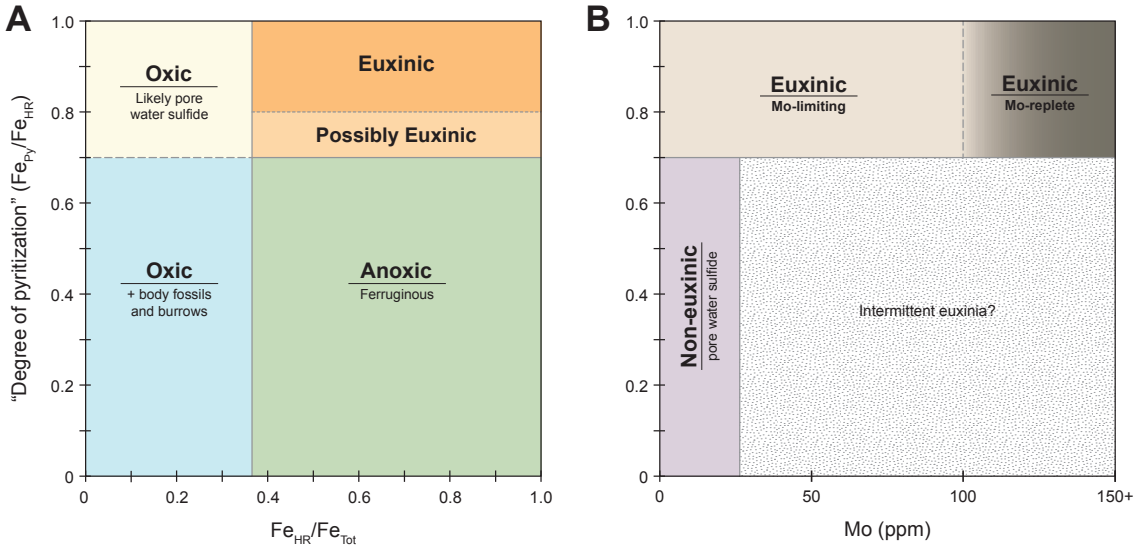
Simple take home:

High Mo (>100 ppm) = High TOC and euxinia

Low Mo is non-unique

Oxic or ferruginous environment with low TOC
Ferruginous environment with economic levels of TOC
Euxinic with very high TOC

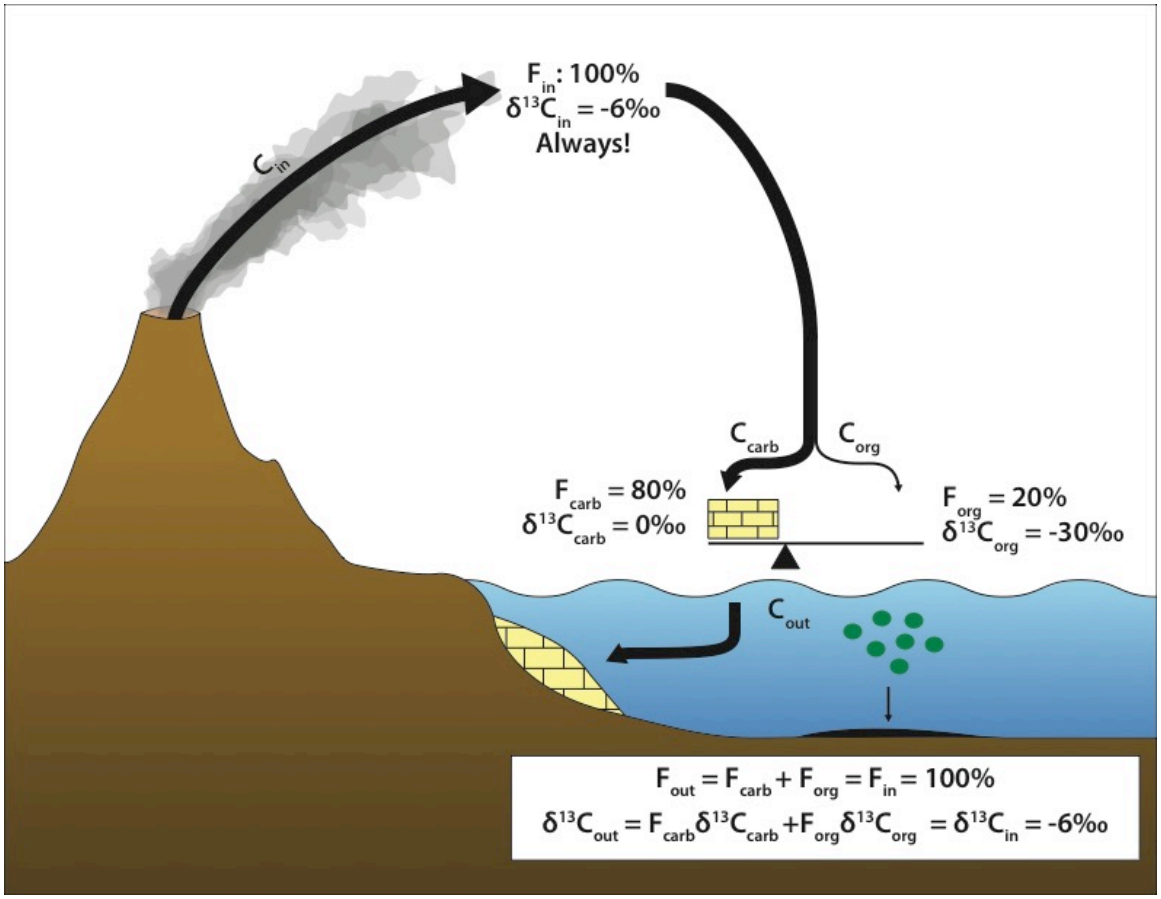
Although high Mo concentrations do positively fingerprint high TOC and euxinic conditions in almost all cases, low Mo concentrations are non-unique. They could represent everything from fully oxygenated, low TOC horizons, ferruginous conditions such as in the Utica Shale that still have economic levels of TOC, or euxinic/high TOC conditions with low Mo concentrations resulting from either water-mass restriction or globally widespread reducing conditions.



[after Poulton and Canfield, 2011; Scott and Lyons, 2012; Sperling et al., 2015]

To distinguish between possibilities, the most robust redox interpretation will involve multi-proxy investigation of iron speciation and redox-sensitive trace metals (above).

Carbon isotope chemostratigraphy



Schematic depiction of the carbon cycle (Figure made by SPODDS student Malcolm Hodgskiss). Carbon enters the Earth system through volcanic activity (presumably at a constant isotopic input value through time) and equilibrates with the oceans. Phytoplankton take up carbon during photosynthesis but select the lighter carbon isotope (^{12}C preference). This drives the oceanic carbon pool more positive (^{13}C enriched). If the balance of carbon burial between organic carbon and carbonate carbon shifts towards organic carbon burial, more ^{12}C will be removed from the ocean, and both the carbonate carbon isotope record and the organic carbon isotope record will experience positive carbon isotope excursions (^{13}C enrichment). Negative carbon isotope excursions will result from a proportional decrease in organic carbon burial (although there are other factors that can also drive negative excursions, related to the rapid input of isotopically light carbon into the Earth system). The factors driving specific carbon isotope excursions are a matter of great debate in the geochemistry community, but it is clear that 1) widespread black shales and unconventional targets are often associated with Earth system perturbations, 2) Earth system perturbations are associated with carbon isotope

excursions, 3) these carbon isotope excursions can be used as a correlative tool between and within basins even if we lack a precise mechanistic understanding of their origin.