EGU 2020

Geochemistry of the manganese ore and black shale in the Datangpo Formation

—Implications for the ore genesis and marine redox during the interglaciation of Neoproterozoic Snowball Earth

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1. Introduction

- Basics of the Datangpo Formation
- Two critical questions

2. Enrichment of organic matter

- This study and compiling results
- Provenance characteristics
- Nutrients characteristics

3. Redox after the Sturtian glaciation

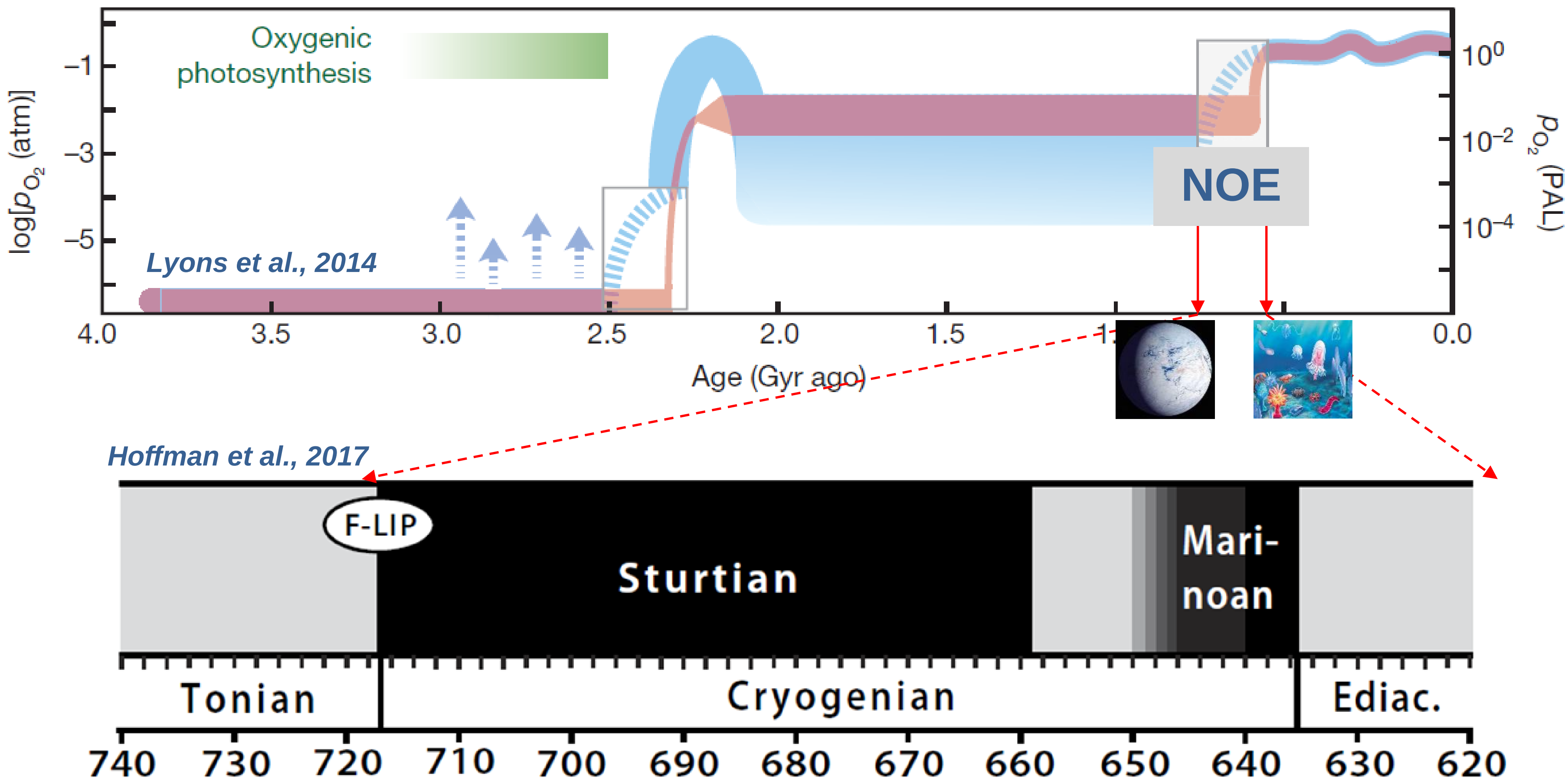
- Elemental evidences
- Mo isotopic evidences

4. Conclusions

1. Introduction

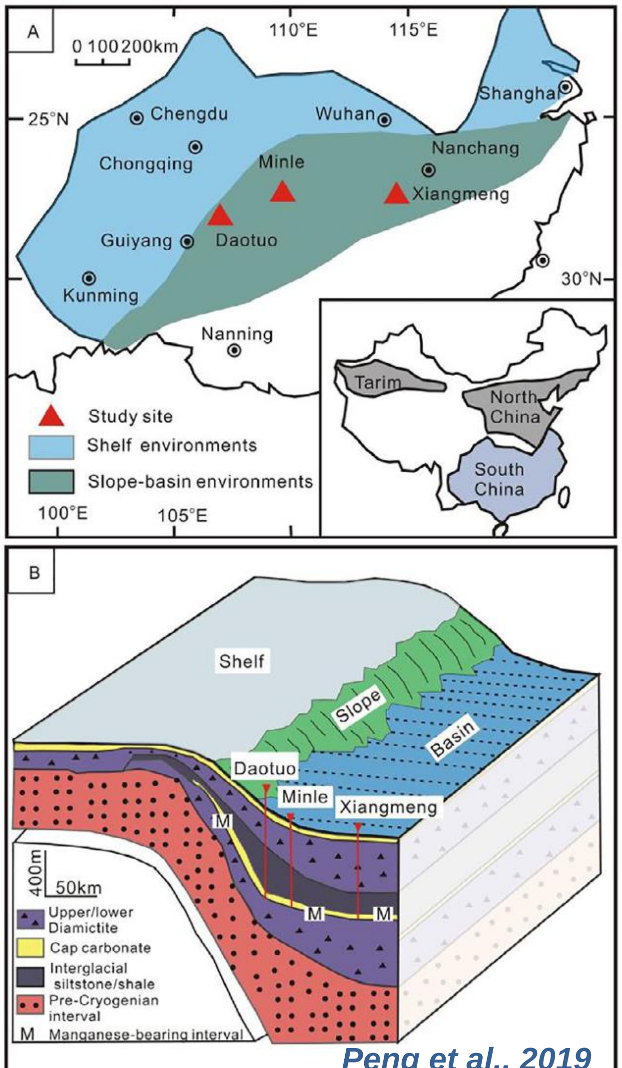
■ Basics of the Datangpo Formation

- **The interglaciation of Snowball: 658.8 – <654 Ma**
- **Early period of Neoproterozoic Oxygenation Event**
- **Basal Mn carbonate and black shale**



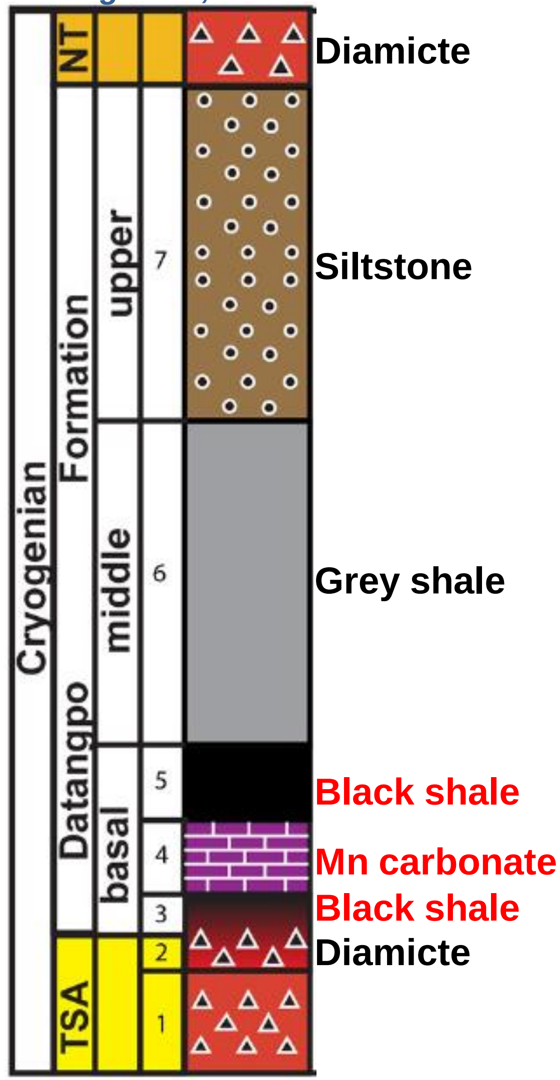
1. Introduction

■ Basics of the Datangpo Formation



Peng et al., 2019

Zhang et al., 2015



Giant Mn-carbonate ore

- Estimated resource: ~4×10^8 t

Location

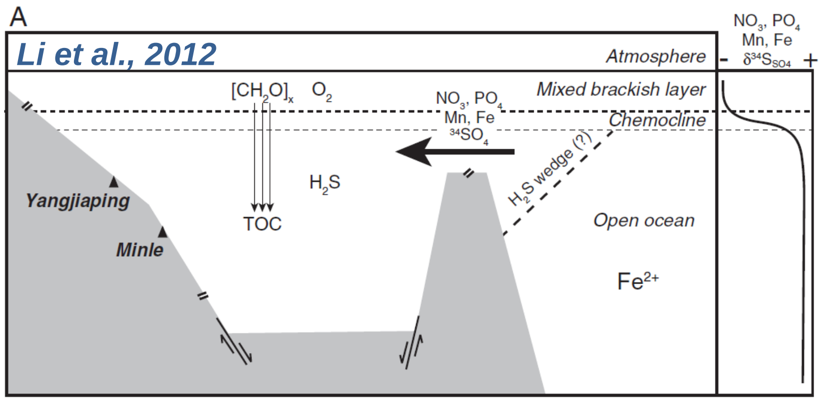
- Yangtze Block, South China
- Mainly in slope to basin facies of the Nanhua Rift Basin (750-500 Ma)

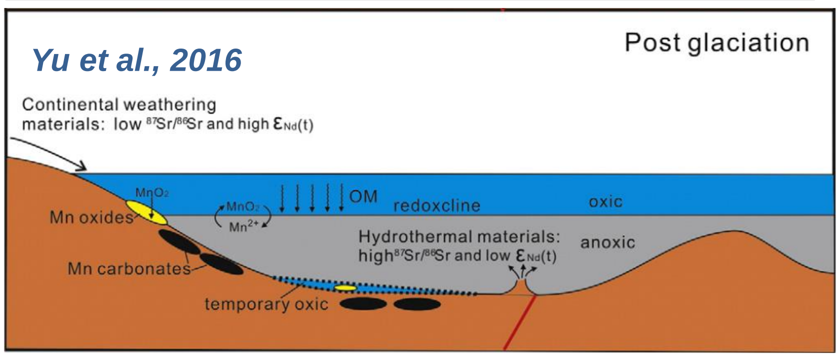
Strata thickness

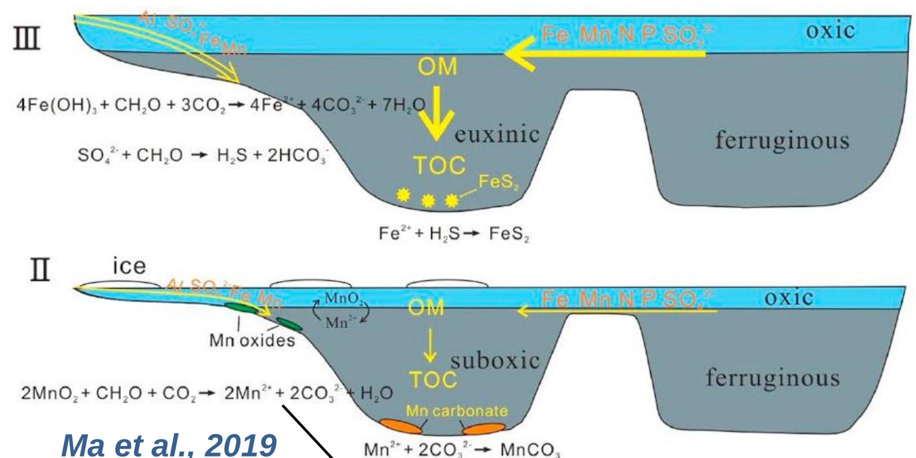
- Controlled by paleobathymetry
- For drill cores, total 90-370 m, Black shale ~tens meters, Mn carbonate ~ a few meters

1. Introduction

■ Two critical questions







Different redox conditions

- Mn carbonate: anoxic with temporal oxic bottom water (?) vs. suboxic
- Black shale: anoxic to euxinic

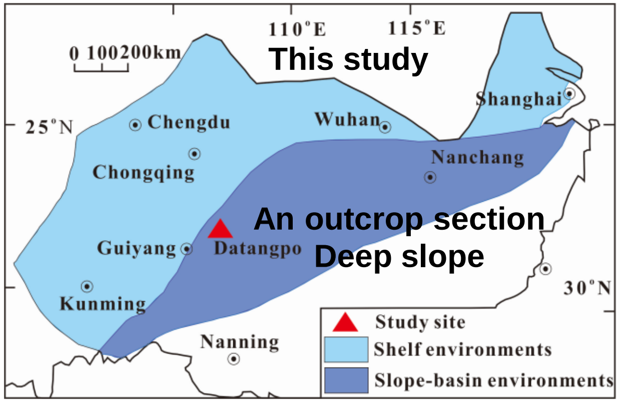
Two-step formation of Mn carbonate

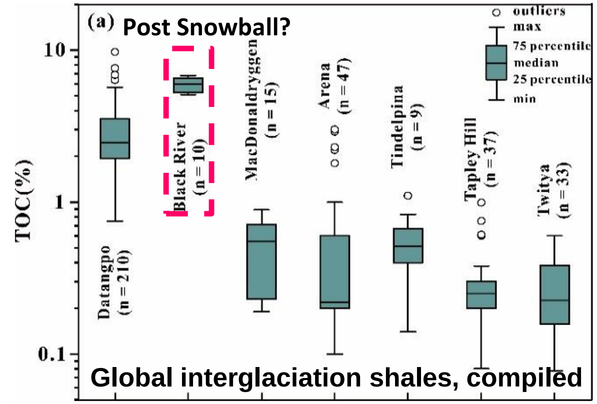
- MnO_2: via autotrophic microbial activity under oxic conditions
- $MnCO_3$: reduction of MnO_2 by heterotrophic microbes under sub-oxic conditions

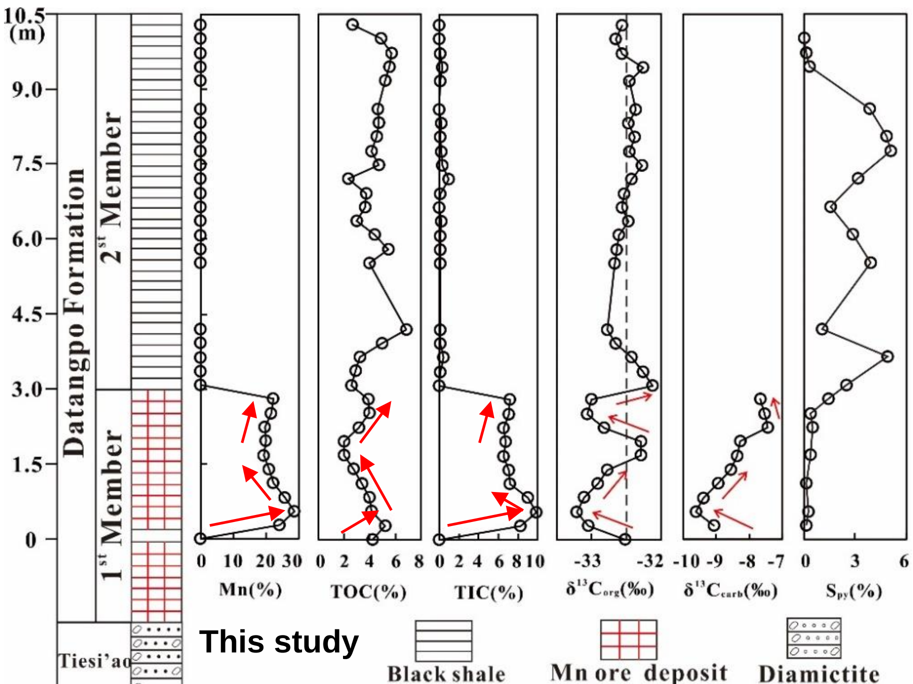
The reduction of MnO_2 and oxidation of OM would result in large decrease in TOC content?

2. Enrichment of organic matter

■ This study and compiling results







Mn carbonate

- ~3 m
- TOC 2.0-5.2%
- Mn 19.4-28.6

Black shale

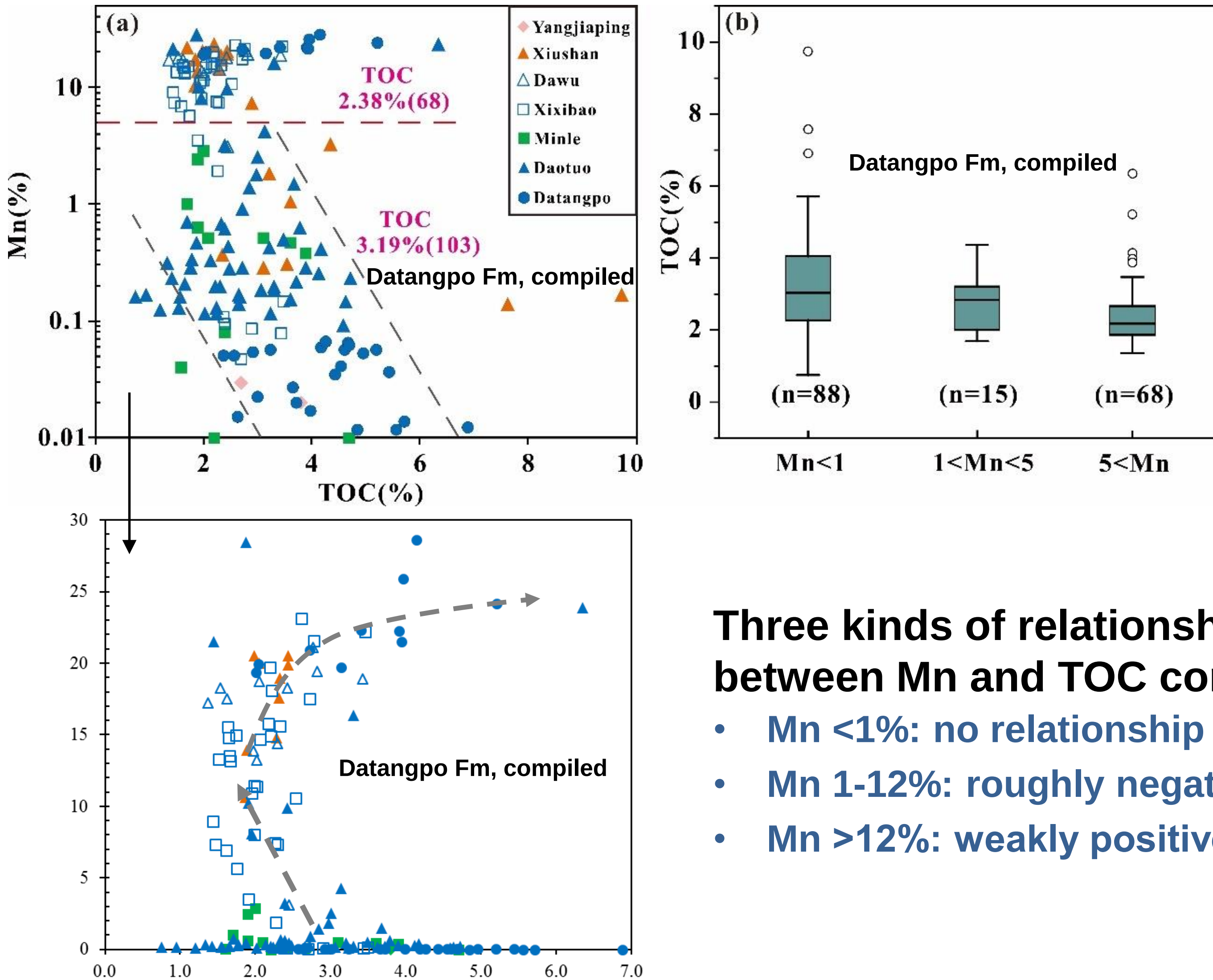
- ~7.5 m
- TOC 2.4-6.9%
- Mn 0.01-0.07%

Two rough co-variations

- Content: Mn–TOC–TIC
- Carbon isotopes: organic–inorganic

2. Enrichment of organic matter

■ This study and compiling results



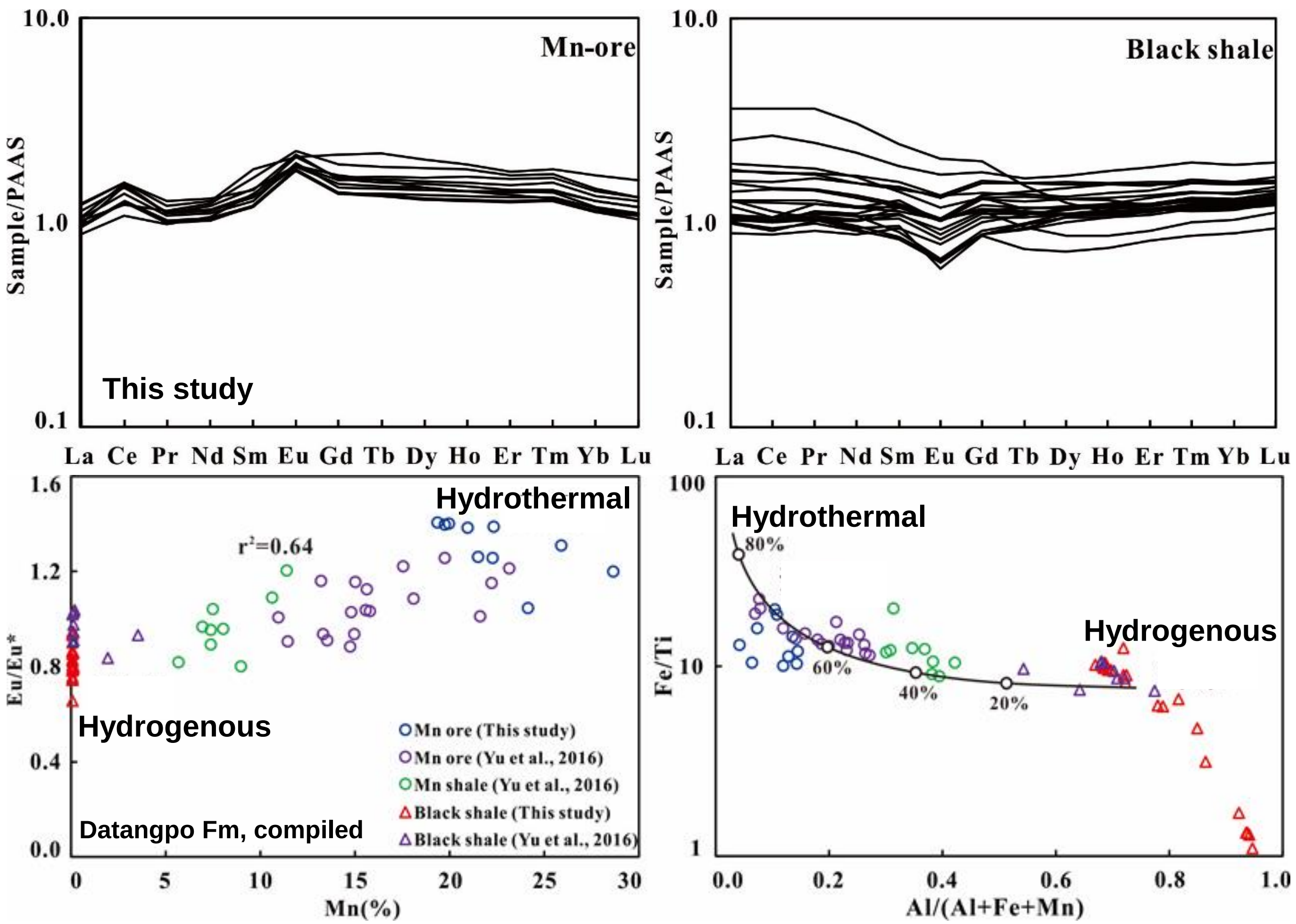
Three kinds of relationships between Mn and TOC contents

- **Mn <1%: no relationship**
- **Mn 1-12%: roughly negative**
- **Mn >12%: weakly positive—Why?**

2. Enrichment of organic matter

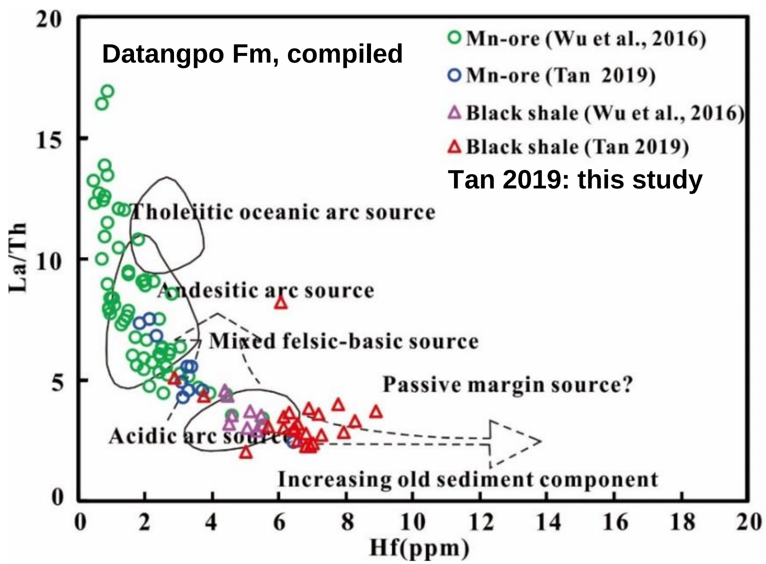
■ Provenance characteristics

- **Mn carbonate: positive Eu*, relatively high abundances of Fe but low Al, etc. suggesting a large contribution from hydrothermal origin**



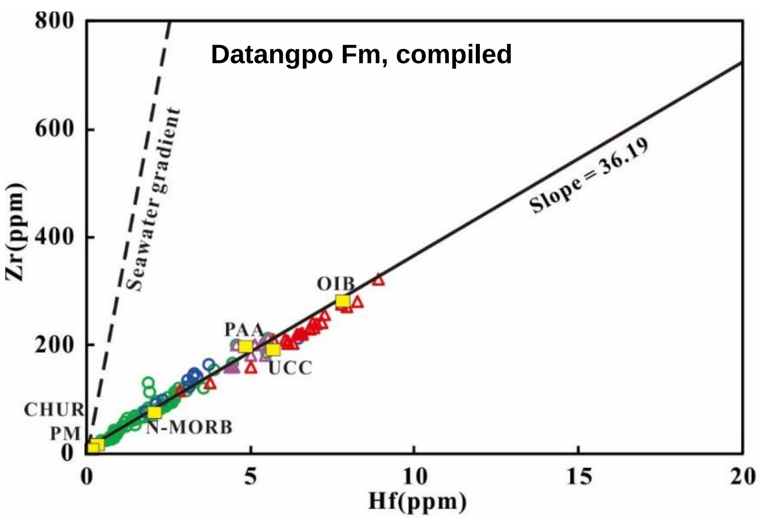
2. Enrichment of organic matter

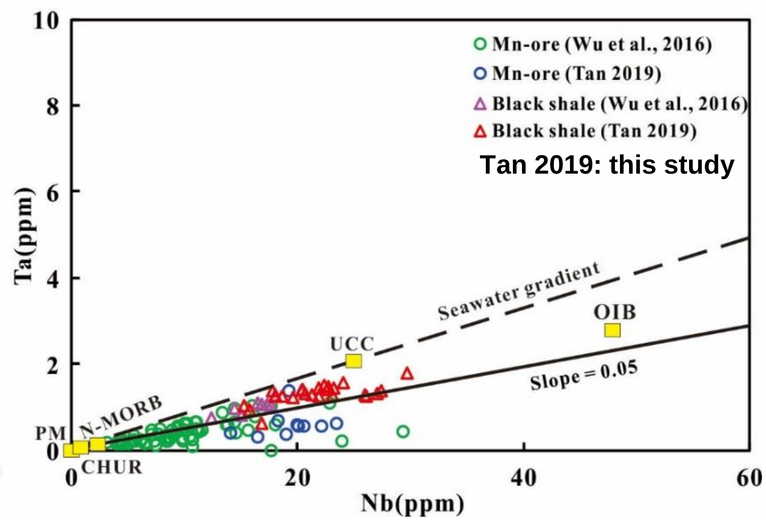
■ Provenance characteristics



Mn carbonate: more mafic than shale

- La/Th vs. Hf：Mn ore in mixed and tholeiitic arc ranges，black shale mainly in acidic arc range
- HFSE abundances: low for Mn ore, close to Primitive Mantle/MORB, while black shale close to Upper Continental Crust/PAAS



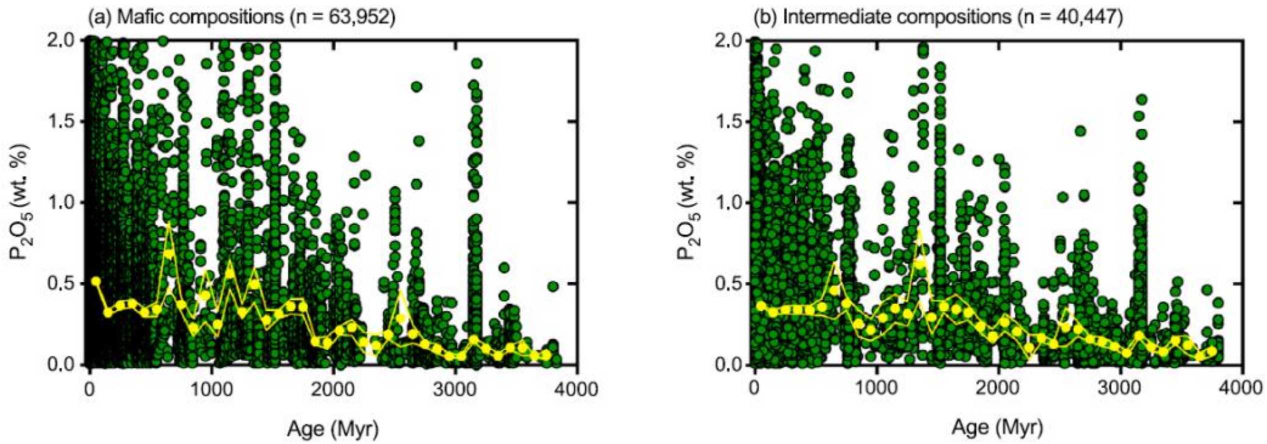


2. Enrichment of organic matter

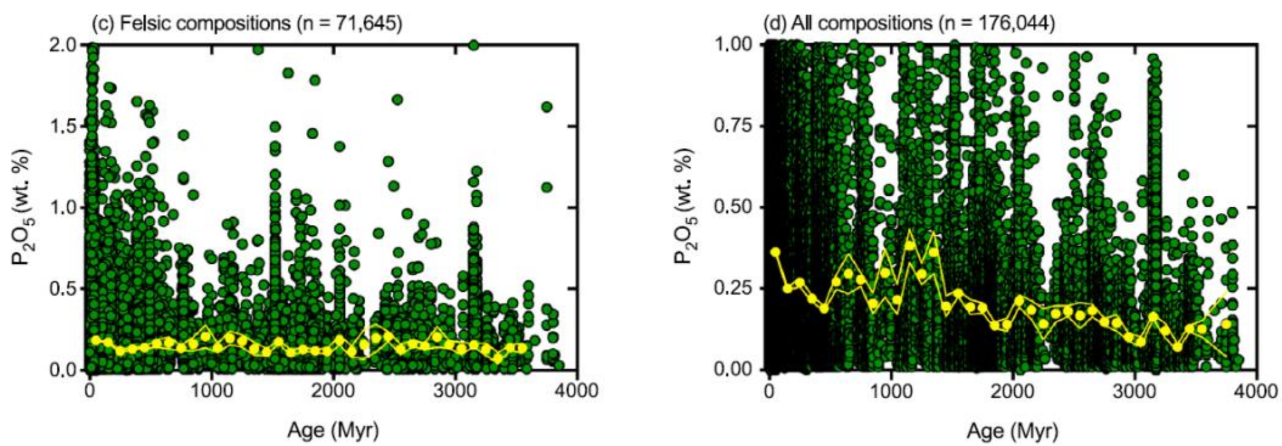
■ Provenance characteristics

More mafic igneous rocks, higher P abundance

"Mafic nutrient pump"–Cox et al., 2016: How abut the Datangpo Fm?



Cox et al., 2016

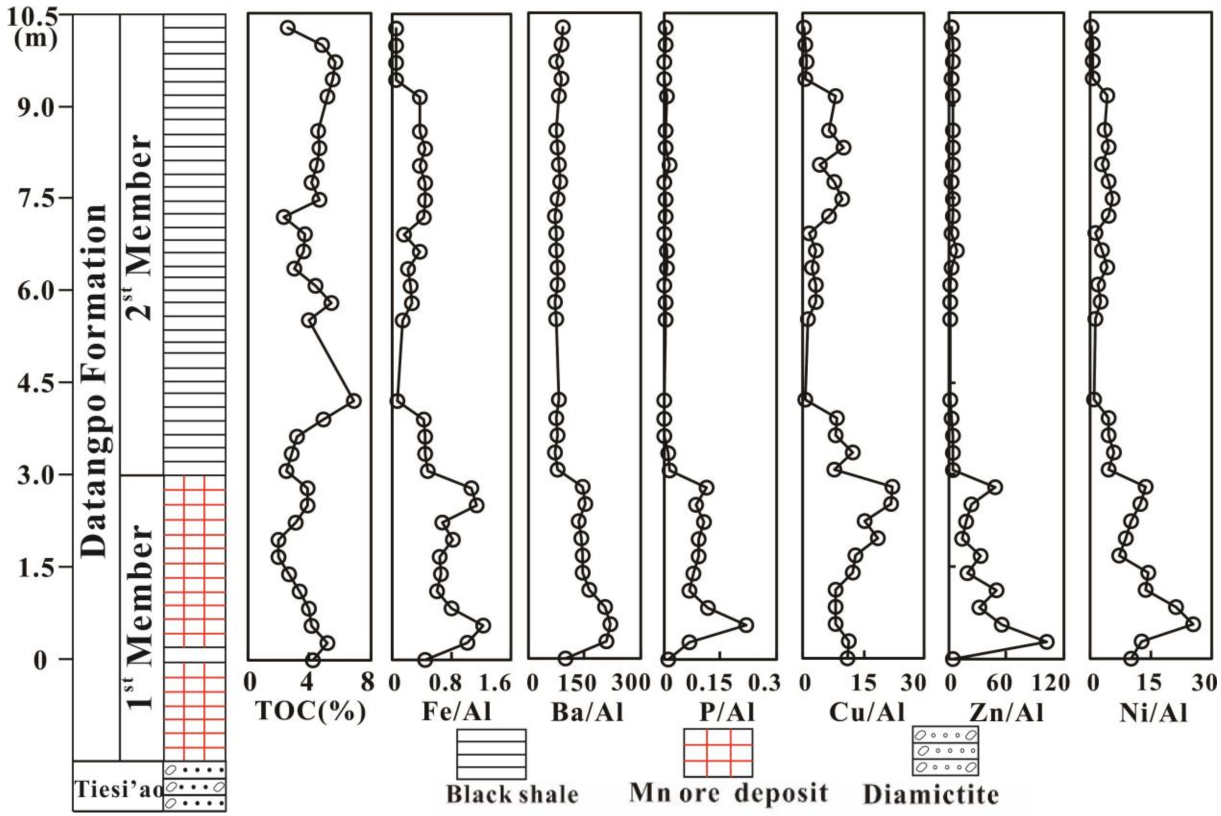


2. Enrichment of organic matter

■ Nutrients characteristics

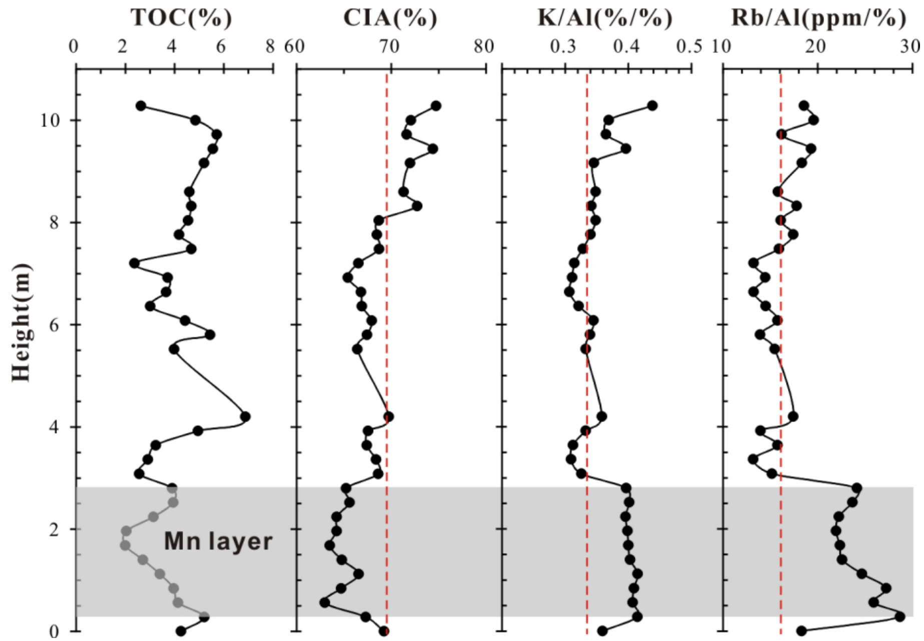
- Ba-P-Fe：redox related, high in Mn carbonate
- Cu-Zn-Ni: organic matter related, also high in Mn carbonate

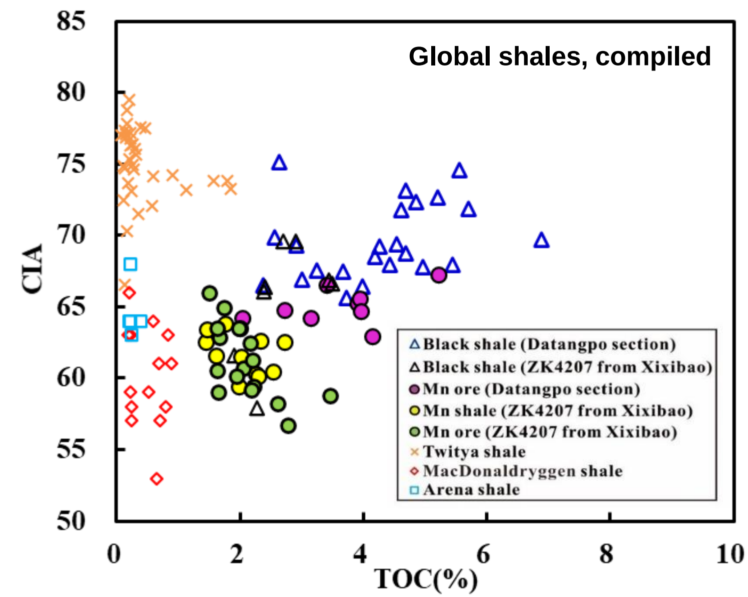
more nutrients in Mn carbonate than in black shale

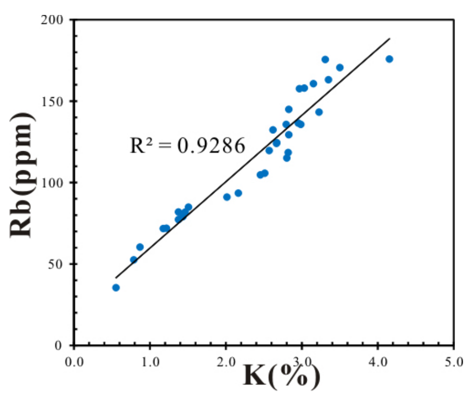


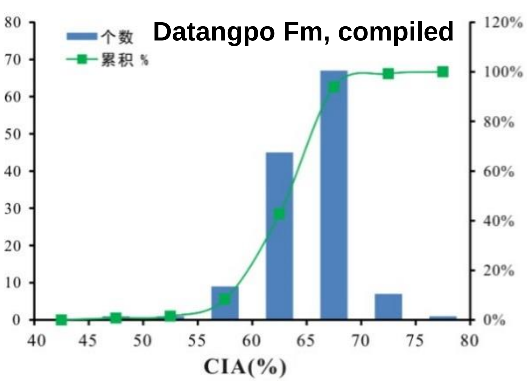
2. Enrichment of organic matter

■ Nutrients characteristics









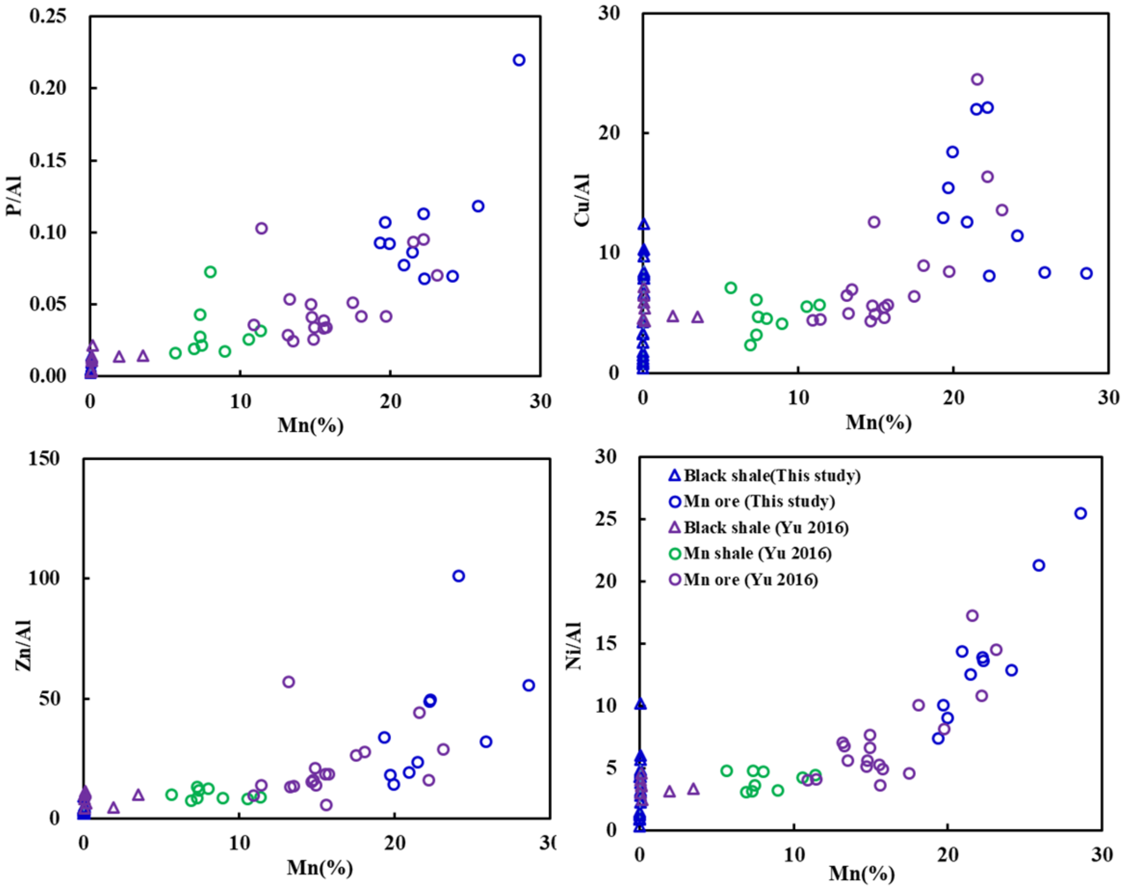
Chemical weathering is not the controlling factor for nutrients' enrichment in Mn carbonate

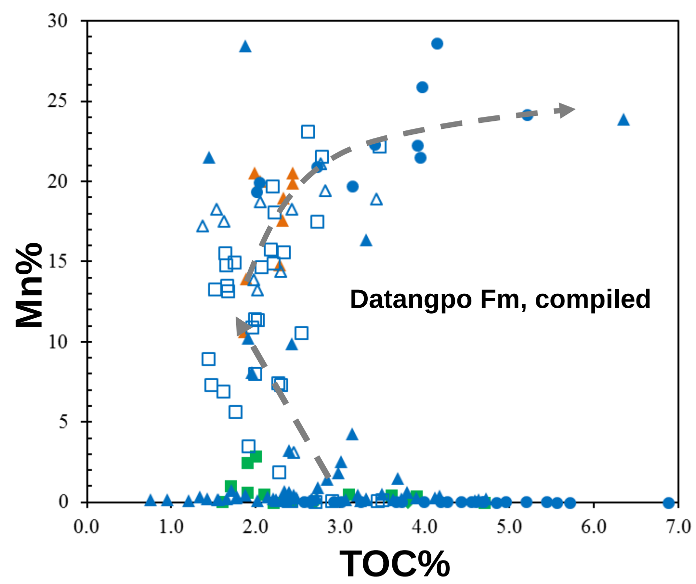
- Overall medium CIA values
- slightly lower CIA for Mn carbonate than black shale, may be affected by lithology difference

2. Enrichment of organic matter

■ Nutrients characteristics

- Nutrient elements: increase with Mn% > ~12
- Could be the cause of relative enrichment in OC with Mn% >12

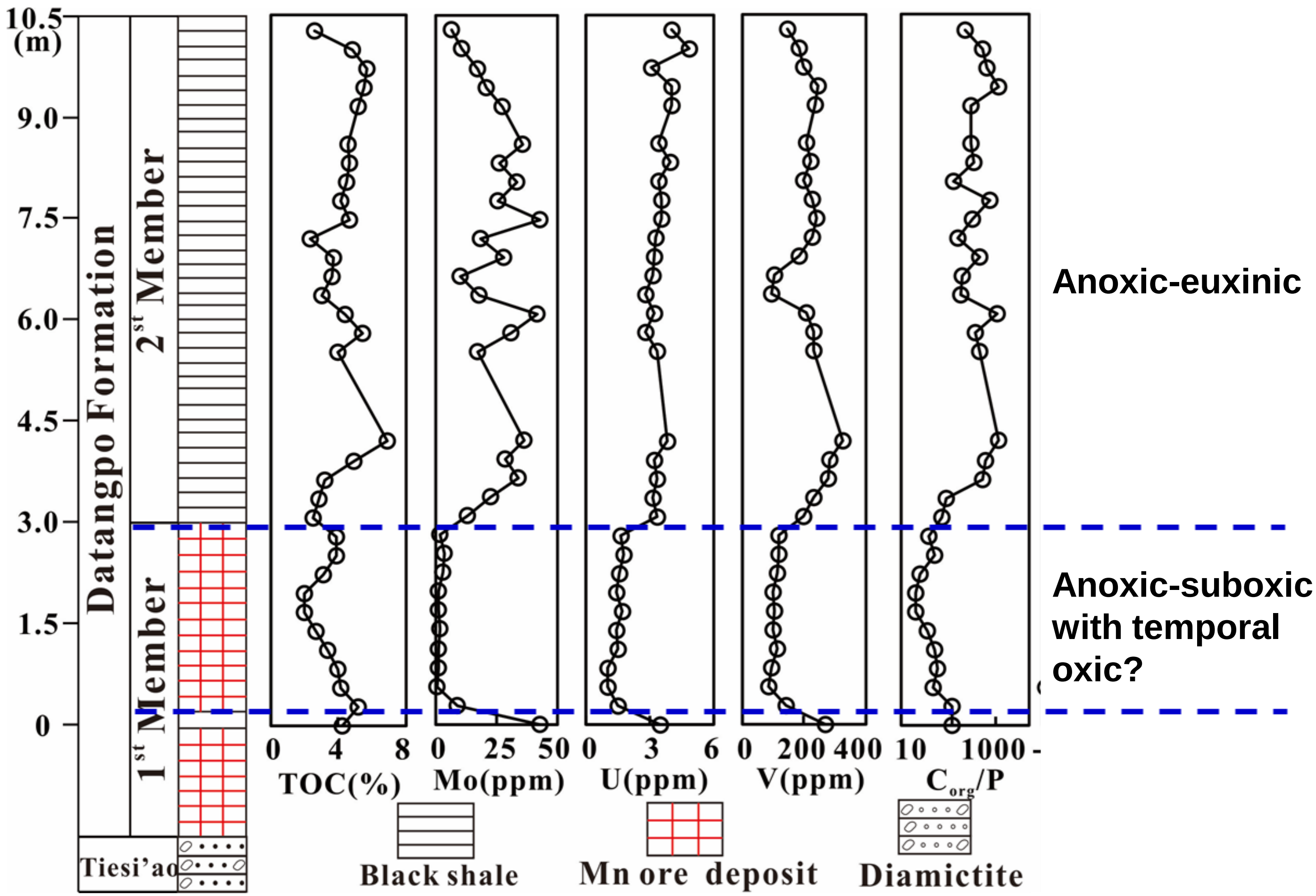




3. Redox after the Sturtian glaciation

■ Elemental evidences

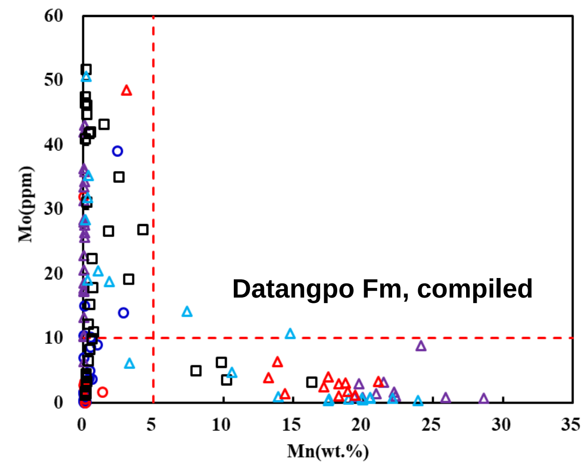
- Distinct between Mn carbonate and black shale

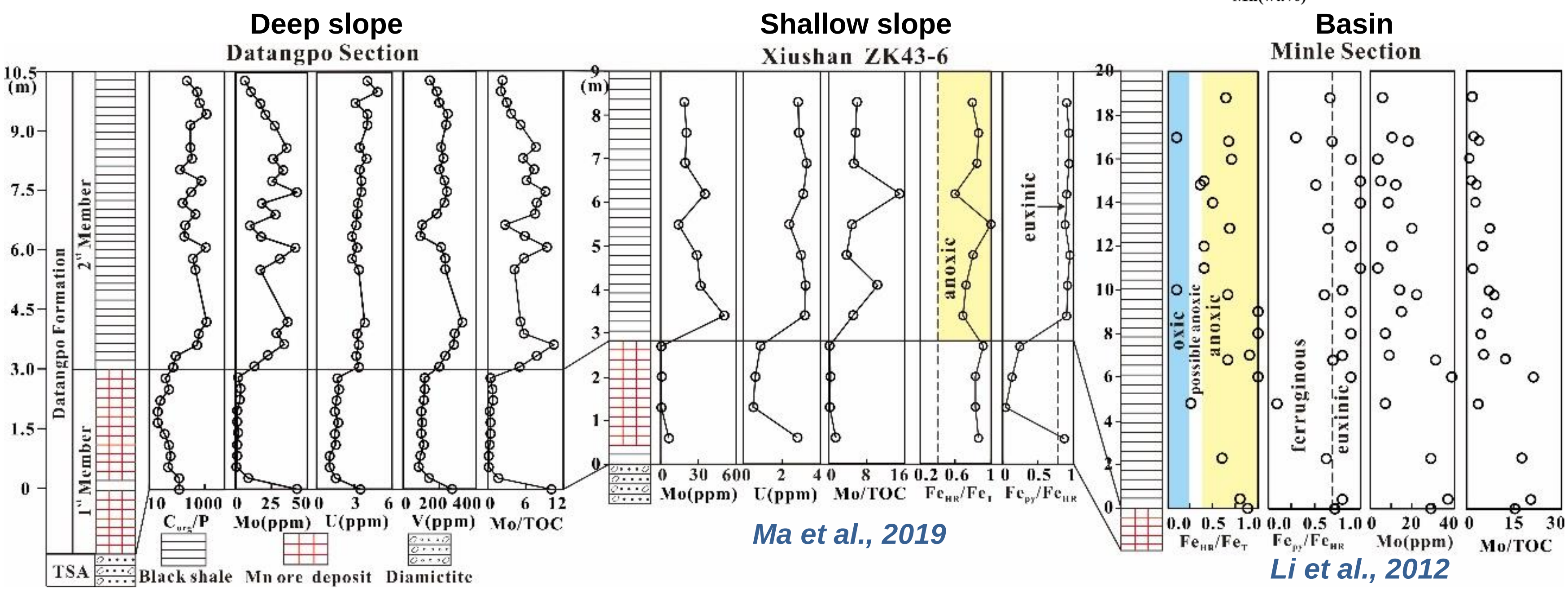


3. Redox after the Sturtian glaciation

■ Elemental evidences

- Black shale: overall euxinic
- Mn carbonate: anoxic-suboxic, **but very low Mo and Corg/P?**





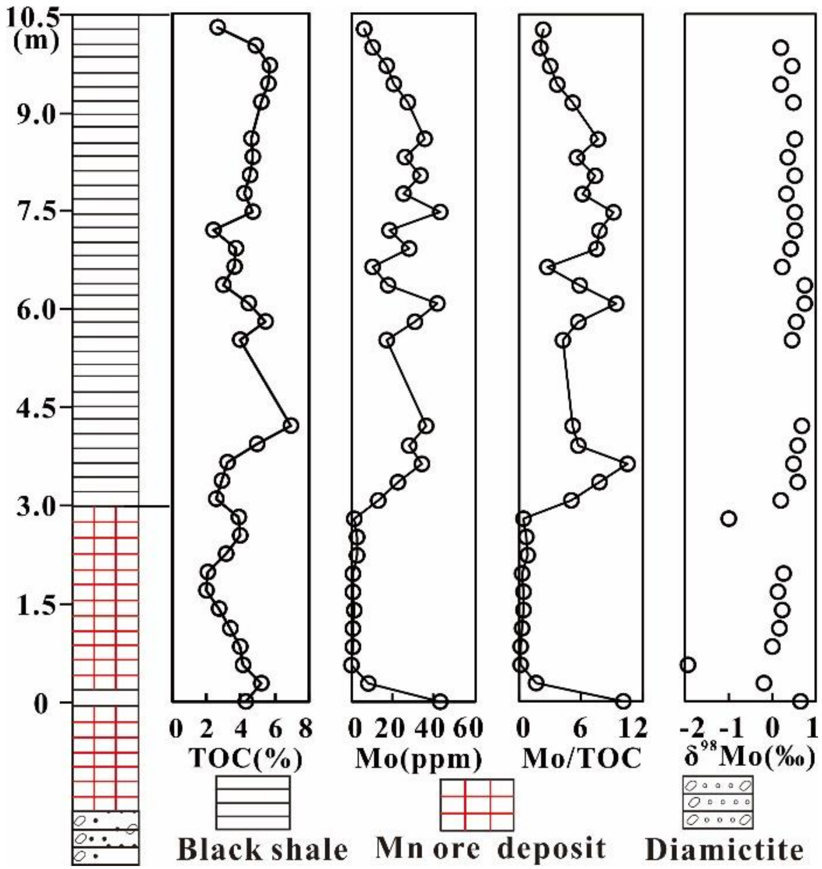
Ma et al., 2019

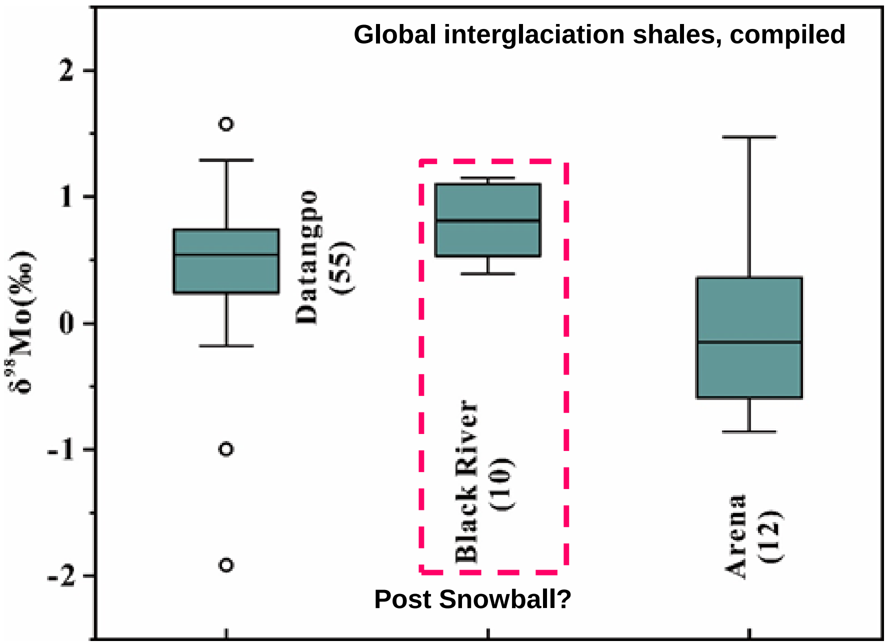
Li et al., 2012

3. Redox after the Sturtian glaciation

■ Mo isotopic evidences

- $\delta^{98}Mo < 1.5‰$, suggesting dominantly anoxic condition in the global ocean during the Neoproterozoic Snowball period (Cheng et al., 2017)

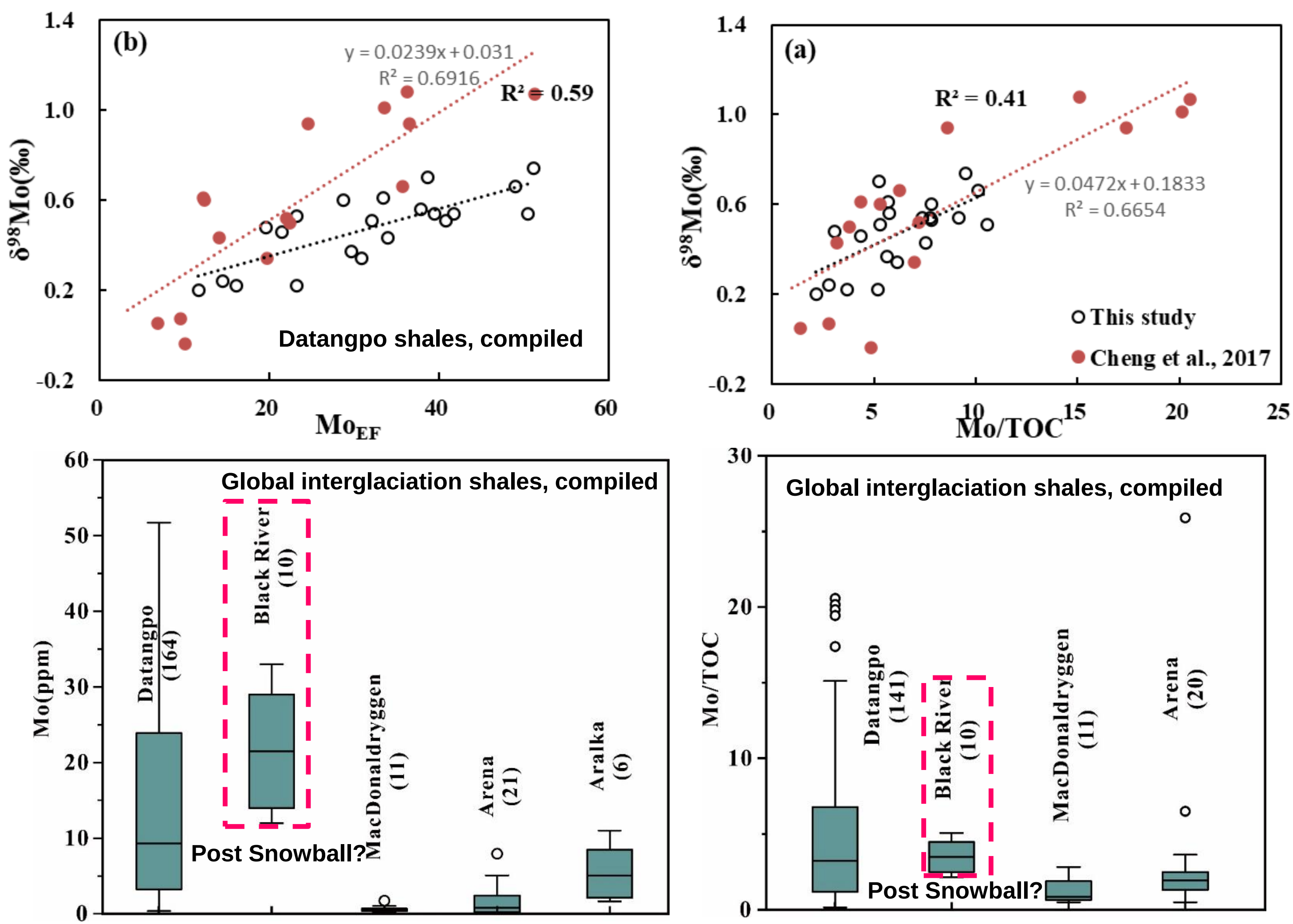




3. Redox after the Sturtian glaciation

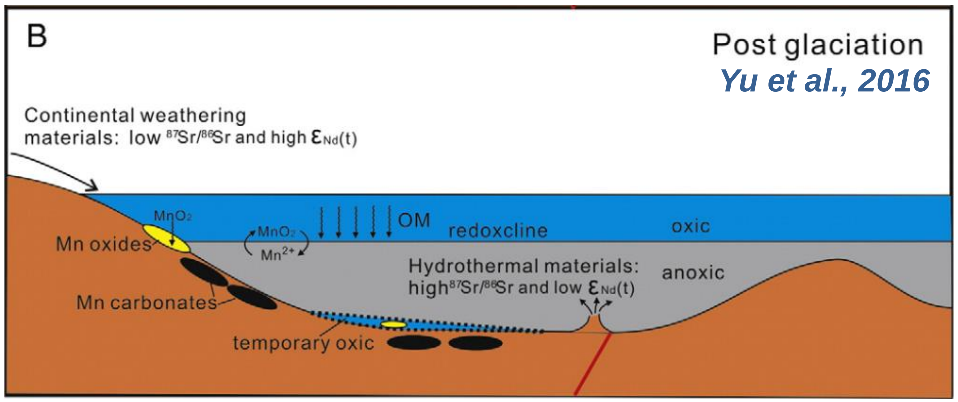
■ Mo isotopic evidences

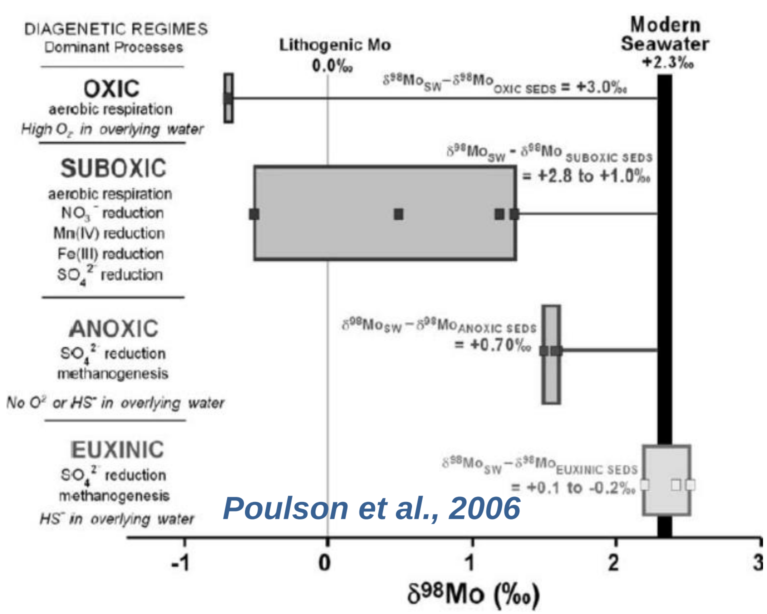
- **Black shale: locally euxinic condition**



3. Redox after the Sturtian glaciation

■ Mo isotopic evidences





Formation of Mn carbonate

- Anoxic bottom water: large amount of hydrothermal sourced P and Mn^{2+}
- Temporary oxic: formation of MnO_2 adsorbing light Mo isotope, low Corg/P ratio is both redox and source controlled
- Suboxic within sediments: reduction of MnO_2 (OM oxidation) to Mn carbonate, releasing most of Mo back into seawater

4. Conclusions

- Both Mn carbonates and black shales of basal interglacial Datangpo Formation contain relatively abundant residual OM (TOC average ~2.5%), compared with other shales of similar ages. Mo isotopes and content of shales suggest the interglacial ocean during Neoproterozoic Snowball period was generally anoxic, which may reflect a relatively low oxygen level and local formation of OM-enriched black shales.
- Notable light $\delta^{98}Mo$ values of Mn ore samples (carbonate) demonstrate episodic bottom water oxygenation may be arose by the influx of high-density ice melting water, which facilitated the formation of Mn oxides in deep water by a microbial process.
- TOC content of Mn-rich samples first decreases with increasing Mn content, but then slightly increase with Mn content higher than ~12%. The decrease in TOC content could be resulted from a oxidation of OM during the reduction of Mn oxides mediated by microbial process, by contrast, many Mn ore samples still having high TOC content may be due to abundant nutrients associated with the hydrothermal fluid that has contributed to a high productivity level.

Thank you for attention!