PS Resetting of Mg Isotopes Between Calcite and Dolomite During Burial Metamorphism: Outlook of Mg Isotopes as Geothermometer and Seawater Proxy*

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Abstract

Carbonate is a common sedimentary rock throughout the earth's history, a significant hydrocarbon reservoir, dutiful recorder for information on sedimentary environment, and diagenesis process it has attracted a lot of attention of geologists. Conventionally, element contents and traditional stable isotope ratios such as carbon and oxygen isotope serve as prime proxies in previous studies. Magnesium isotope is an emerging tool to study the geological processes recorded in carbonates. Calcite, due to its ubiquitous occurrence and the large Mg isotope fractionation associated with the mineral, has attracted great interests in applications of Mg isotope geochemistry. However, the fidelity of Mg isotopes in geological records of carbonate minerals, particularly calcite, remains poorly constrained. Here we systematically investigated the dolomitized Middle Triassic Geshan carbonate section in eastern China. Multiple lines of evidence consistently indicate that post-depositional diagenesis of carbonate minerals occurred in the carbonate rocks. Magnesium isotope compositions of the carbonate rocks closely follow a mixing trend between a high δ26Mg dolomite end member and a low δ26Mg calcite end member, irrespective of sample positions in the section and calcite/dolomite ratio in the samples. Based on fitting of the measured Mg isotope data using a two-end member mixing model, an inter-mineral $\Delta 26Mg_{dolomite-calcite}$ fractionation of 0.72‰ was obtained through an optimization approach. Using the experimentally derived Mg isotope fractionation factors for dolomite and calcite, a temperature of 150-190 degrees centigrade was calculated to correspond the 0.72‰ $\Delta 26Mg_{dolomite-calcite}$ fractionation. Such temperature range matches well with the burial-thermal history of the local strata, making a successful case of Mg isotope geothermometry. Our results indicate that both calcite and dolomite had been equilibrated with a common fluid during burial diagenesis, and based on mass balance such fluid should have been buffered by dolomite from the section. Therefore, burial diagenesis may reset Mg isotope signature of calcite, and Mg isotope compositions in calcite should be dealt with caution in studies of carbonate rocks with thermal history. By contrast, Mg isotopes of dolomite are less prone to diagenetic resetting due to its high abundance in Mg, and Mg isotopes in dolomite may be a more robust recorder for original precipitates.

References Cited

Hu, Z., W. Hu, X. Wang, Y. Lu, L. Wang, Z. Liao, and W. Li, 2017, Resetting of Mg Isotopes Between Calcite and Dolomite During Burial Metamorphism: Outlook of Mg Isotopes as Geothermometer and Seawater Proxy: Geochimica et Cosmochimica Acta, v. 208, p. 24-40.

Li, W., B.L. Beard, C. Li, H. Xu, and C.M. Johnson, 2015, Experimental Calibration of Mg Isotope Fractionation Between Dolomite and Aqueous Solution and Its Geological Implications: Geochimica et Cosmochimica Acta, v. 157, p. 164-181.

Mavromatis, V., Q. Guatier, O. Bosc, and J. Schott, 2013, Kinetics of Mg Partition and Mg Stable Isotope Fractionation During Its Incorporation in Calcite: Geochimica et Cosmochimica Acta, v. 114, p. 188-203.

Resetting of Mg isotopes between calcite and dolomite during burial metamorphism: Outlook of Mg isotopes as geothermometer and seawater proxy

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Introduction

Carbonate is ubiquitous on Earth, and its element and C-O-Sr isotope compositions have been extensively used to study paleo-environments. Magnesium isotopes are an emerging tool to study the geological processes recorded in carbonates. Calcite, due to its ubiquitous occurrence and the large Mg isotope fractionation associated with the mineral, has attracted great interests in applications of Mg isotope geochemistry. However, the fidelity of Mg isotopes in geological records of carbonate minerals against burial metamorphism remains poorly constrained. Here we the Mg isotope systematics within a Middle Triassic carbonate section from Southeast China to investigate the Mg isotope variability during diagenesis.

Geological Backgrounds

The study area is located at Yixing City, in Lower Yangtze Block of Southeast China. Excellent outcrops of Zhoucunchong Formation, early Anisian of Middle Triassic (~247Ma), are exposed as quarry mining sites at Geshan. Locally, the Zhoucunchong Formation is about 150m in thickness and consists of carbonates ranging from limestone to dolostone, and interbeded gypsiferous rock. Carbonates in the lower Zhoucunchong Formation are variably dolomitized, where limestone, dolomitic limestone, limy dolostone, and dolomstone layers co-exist and interbed each other without hiatus.

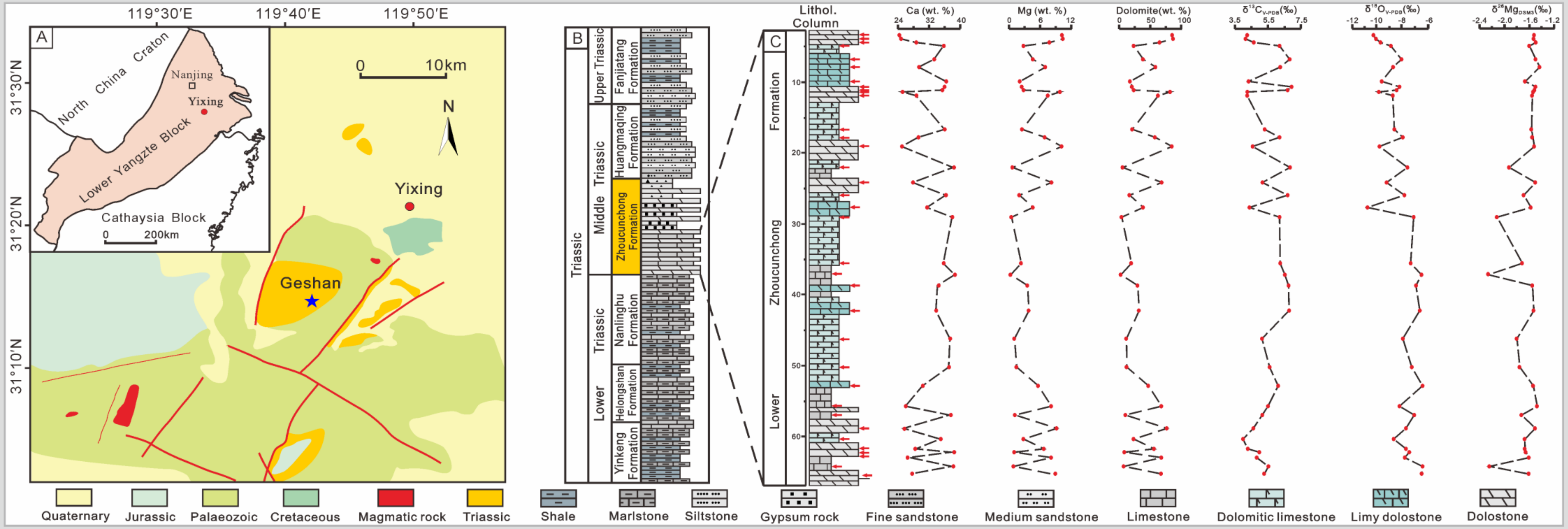


Figure 1. Geological map showing sampling site and the Triassic stratigraphy of the Lower Yangtze Block. (A) Map showing the section and outcrop; (B) Stratigraphic column of Triassic in Lower Yangtze Block; (C) Detailed stratigraphy of the Lower Zhoucunchong Formation in Geshan section,accompanied with major elements, mineral contents and stable isotope compositions.

Petrography and mineralogy

Limestone at outcrops shows dark grey color, whereas dolostone shows light grey color and they interbed each other. Gypsum concretions and nodes occur in dolostone layers. Irrespective of calcite to dolomite ratios, the carbonate samples consistently show micro-crystalline textures, composed of 20-30μm sized calcite crystals and 25-50μm sized dolomite crystals, demonstrating the chemical homogeneity of dolomite and calcite in all Geshan samples and provides the basis for the two end-member mixing concept. The dolomite crystals are mostly subhedral in shape, but the etched edges of some dolomite crystals, indicate dissolution of the originally more euhedral dolomite crystals, implying that a process of dedolomitization may have taken place after the formation of dolomite crystals.

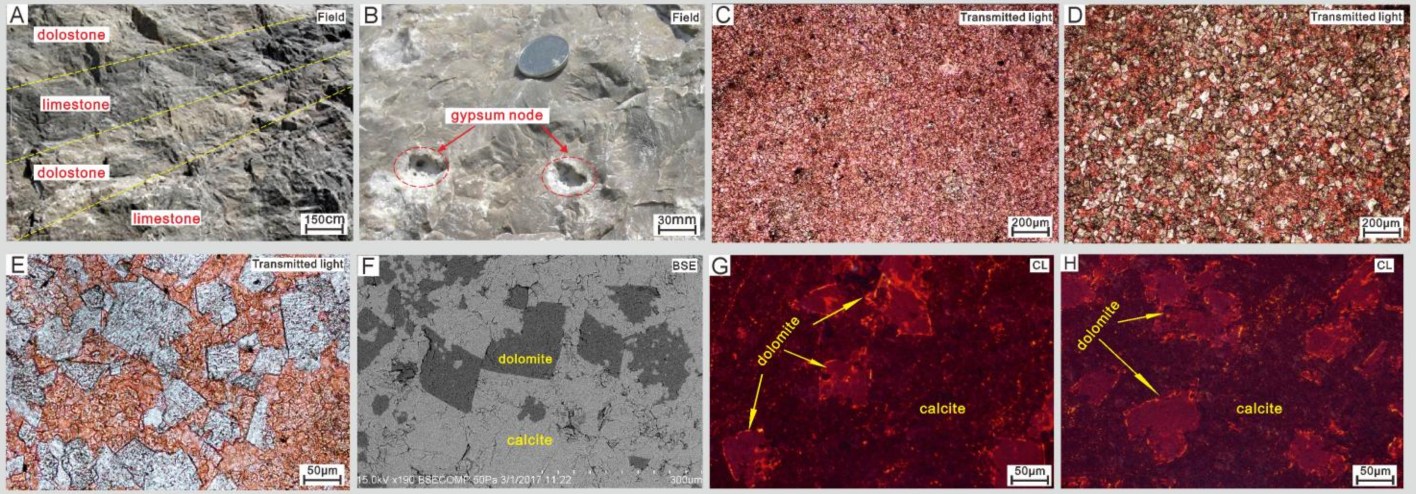
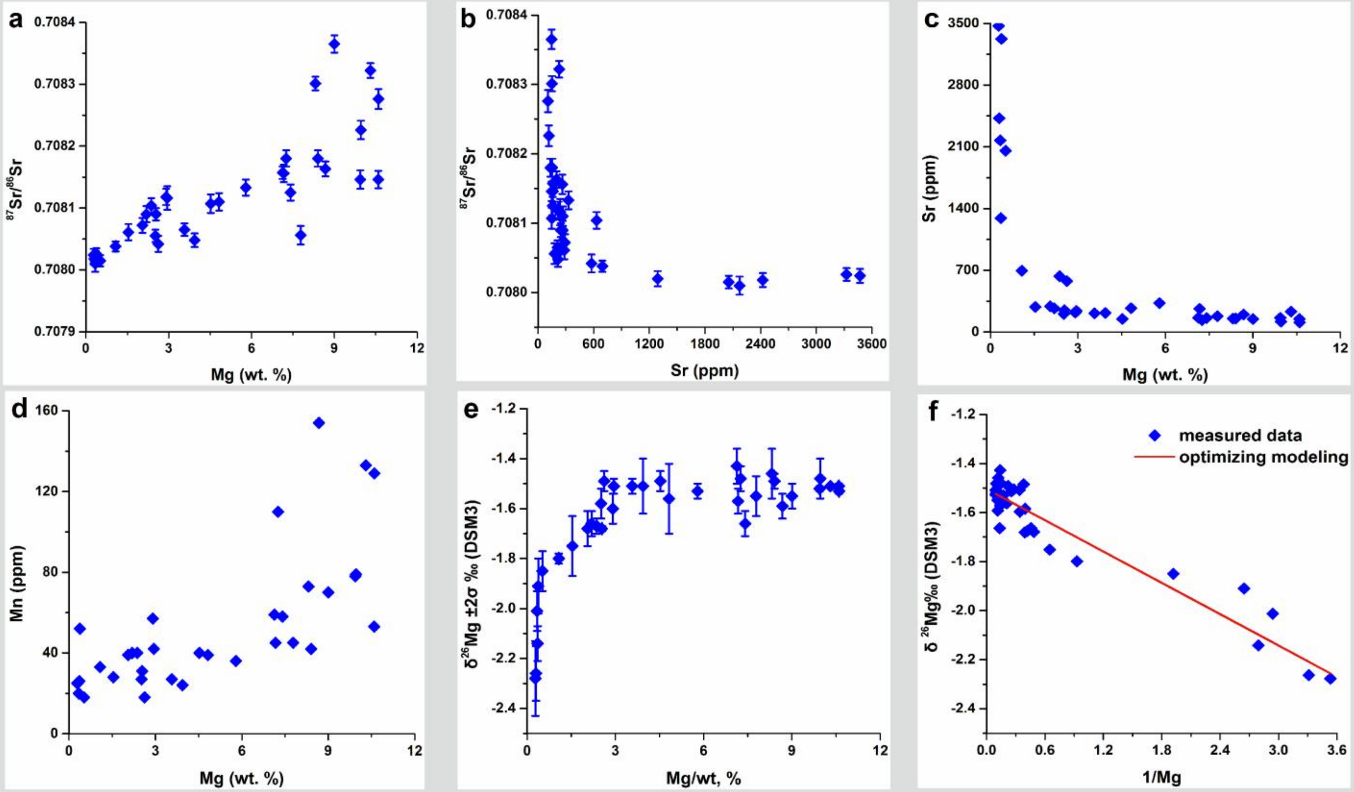


Figure 2. Photographs showing the petrographic characteristics of Zhoucunchong Formation.(A) Limestone and dolomite interbed each other; (B) Gypsum node replaced by sparry calcite; (C) Limestone (ZC-26); (D) Limy dolomstone (ZC-28); (E) Dissolution texture of dolomite (ZC-28); (F) Back scattering image of dissolution texture of dolomite (ZC-22); (G-H) Cathodoluminescence photomicrograph of dissolution texture of dolomite (ZC-14).

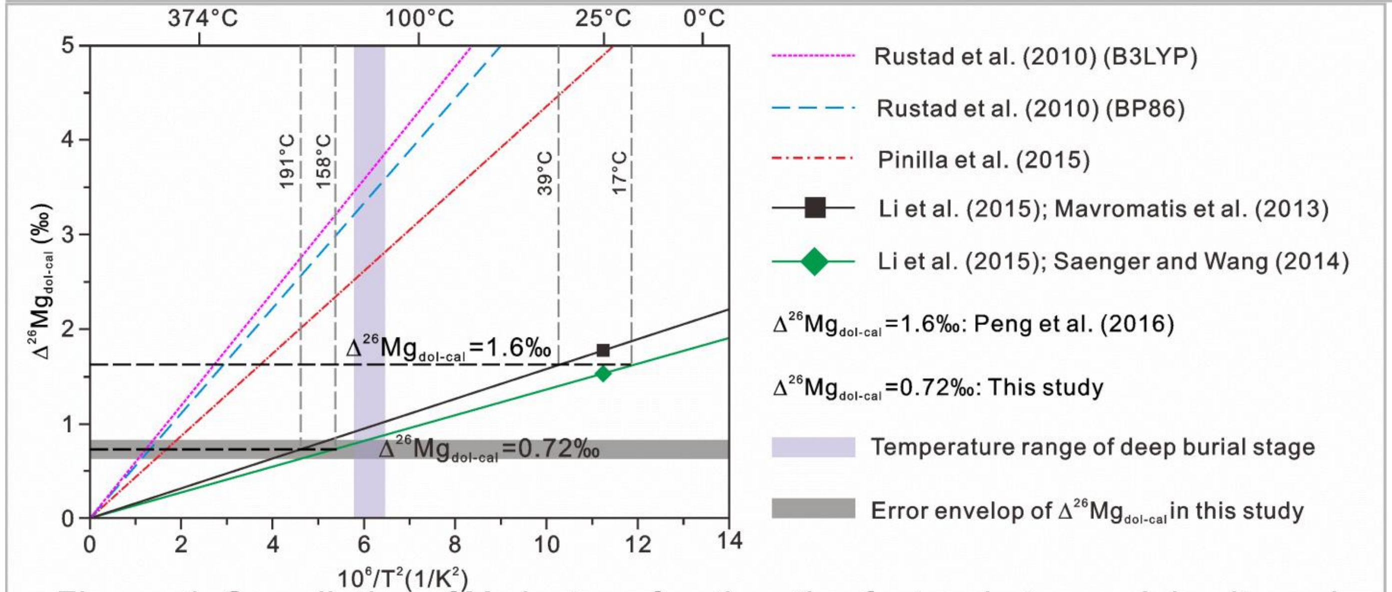
Geochemistry

Cross-plots of Sr versus Mg contents also support two end member mixing, together with the positive correlation between Mn and Mg, indicate calcite has low Mn content and high Sr content whereas dolomite has high Mn content and low Sr content. The higher $^{87}Sr/^{86}Sr$ ratios of dolomite-rich carbonates, however, are attributed to relatively higher contributions of radiogenic ^{87}Sr in the low Sr dolostone samples, whereas carbonates with high Sr concentrations are considered to be less impacted by radioactive decay of ^{87}Rb from detrital components .Magnesium isotope compositions in Geshan carbonates also show distinct feature of two end member mixing, as indicated by the linear relation between Mg isotope ratios and the reciprocal of Mg contents.

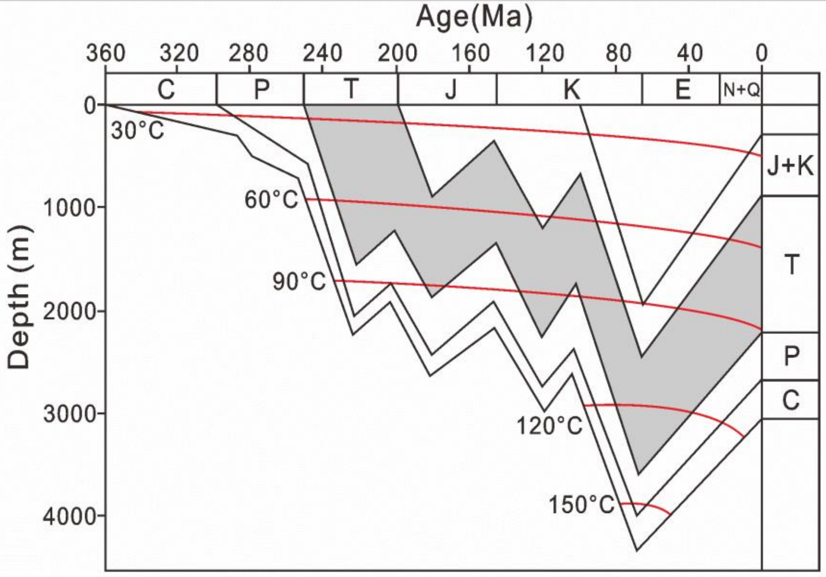


Applicability of Mg isotopes in carbonate minerals as seawater proxy

The 0.72‰ difference in $\delta^{26}Mg$ between the dolomite end member and the calcite end member of Geshan section is remarkably smaller than the 1.6‰ difference in $\delta^{26}Mg$ between calcite anddolomite in the previous study that was interpreted to reflect precipitation at a low temperature, reflecting inter-mineral Mg isotope fractionation at an elevated temperature. A temperature of 150-190ºC was calculated to correspond to the 0.72‰ $\Delta^{26}Mg_{dolomite-calcite}$ fractionation. Such temperature range matches with the local burial-thermal history, making a successful case of Mg isotope geothermometry. Multiple lines of evidence show that burial metamorphism may reset Mg isotope signature of calcite, Mg isotopes of dolomite are less prone to post-depositional resetting due to a number of properties and may be a more robust recorder for original carbonate precipitates.Magnesiumisotope fractionation factors for carbonate minerals have been investigated by a number of workers, using approaches of theoretical calculation or experimental calibration. Large discrepancies, however, exist between the available studies. The experimental study of Marvromatis et al. (2013) is preferred over other studies on calcite due to the better control of kinetic isotope effects and the experimental calibration of Li et al. (2015) more closed to the reality of this study.



Firgure 4. Compilation of Mg isotope fractionation factors between dolomite and calcite as a function of $1/T^2$.



Firgure 5. The burial history of Jurong area near Geshan in the Lower Yangtze Block

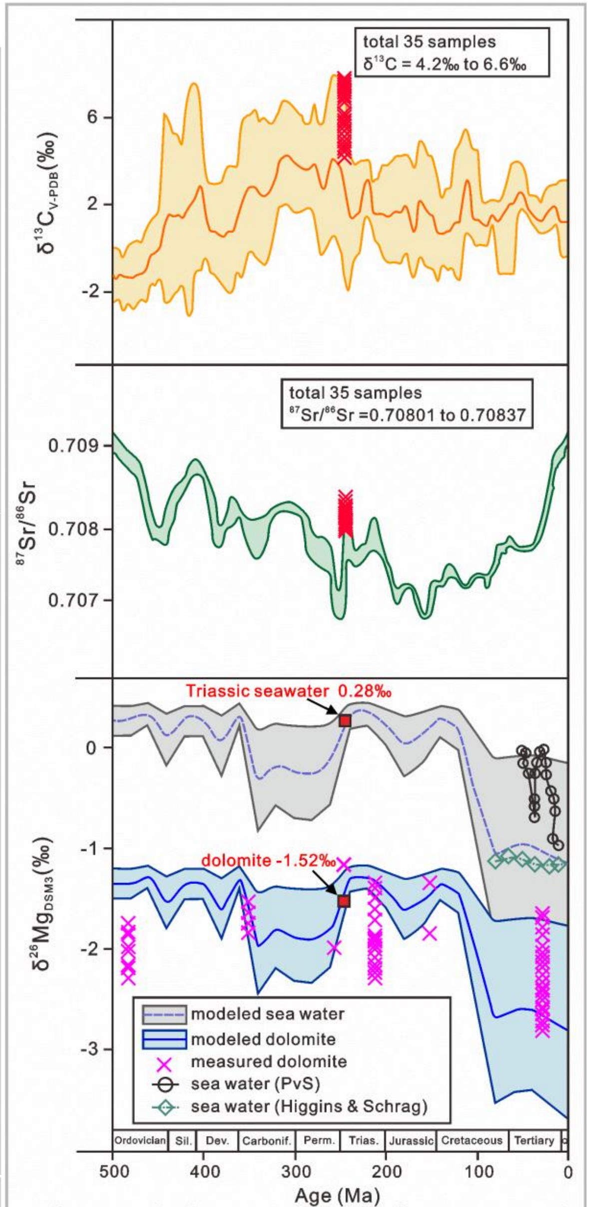


Figure 6.Comparison of measured $\delta^{13}C$, $^{87}Sr/^{86}Sr$ data from Geshan, and the proposed values of seawater over Phanerozoic, as well as a comparison of $\delta^{26}Mg$ of dolomite endmember and corresponding seawater.

Li W., Beard B. L., Li C., Xu H. and Johnson C. M. (2015) Experimental calibration of Mg isotope fractionation between dolomite and aqueous solution and its geological implications. *Geochim. Cosmochim. Acta* 157, 164-181.

Mavromatis V., Gautier Q., Bosc O. and Schott J. (2013) Kinetics of Mg partition and Mg stable isotope fractionation during its incorporation in calcite. Geochim. Cosmochim. Acta 114, 188-203.

Hu Z., Hu W., Wang X., Lu Y., Wang L., Liao Z. and Li W. (2017) Resetting of Mg isotopes between calcite and dolomite during burial metamorphism: Outlook of Mg isotopes as geothermometer and seawater proxy. *Geochim. Cosmochim. Acta* accepted