# New dating result of the Caledonian granitoids and related mineralization of Miaoershan-Yuechengling area, South China

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It has been accepted that W-Sn-(Mo) rare metal mineralization in South China are in close association with the Yanshanian granites, whereas the granites of the other ages results in minor metallogenic process. The effect of Caledonian granites on such kind ore deposits is considered to be neglectable. However, more than 100 mineralization pots and deposits are recently found around Miaoershan-Yuechengling area, which are hosted in Indosinian and Caledonian granitoids. This report presents three typical mineralization samples in Luchongping, Shengxianyan and Niutangjie with dating results of host granites and ore minerals.

(1) Luchongping deposit is of greisen-quartz vein type W-Cu mine in the middle south of Miaoershan. The host rock is a middle-fine grained biotite granite with zircon date of 396-402 Ma; (2) Shenxianyan develops a greisen type W-Mo deposit in the south Miaoershan. The host rock is also the middle-fine grained biotite granite with zircon date of 433.5 Ma; (3) Niutangjie is a strata-banded scheelite deposit of skarn type in the southwest margin of Yuechengling. This deposit is a relatively large ore deposit in this area, which has been mined tens of years. Its host rock is fine-grained muscovite granite. The zircon dating results is 411-422 Ma. The mineralization age is 421±24 Ma.

Based on the above dating results, it it suggested that the Caledonian mineralization is of great importance in the studied area. It is revealed that the primary host rocks are those middle-fine grained biotite granites and the major ore mineral is scheelite. This mineralization feature has already been identified from the Yanshanian metallegenic process in the central Nanling area, South China, where the host rock is mainly fine-grained muscovite granite and the major ore mineral is wolframite.

# Isotope fractionation by alternative nitrogenases and oceanic anoxic events

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The $^{15}N/^{14}N$ of marine N (quantified by the parameter $\delta^{15}N$) is used to reconstruct the N cycle in the modern and ancient oceans[1]. Anomalously low $\delta^{15}N$ values reaching -5‰ have been measured in sediments from mid-Cretaceous oceanic anoxic events (OAEs)[2,3]. These low values, which fall below that of newly fixed N from $N_2$ fixation (currently believed to average -1‰), cannot be explained by current isotopic models .

We show that the $\delta^{15}N$ of newly fixed N can be as low as -7‰, depending chiefly on the type of nitrogenase that catalyzes $N_2$ fixation. Alternative nitrogenases, which contain catalytic vanadium (V) or iron (Fe) rather than molybdenum (Mo), produce fixed N that is significantly lighterin $^{15}N$ than canonical Mo enzymes (-6‰ for V-, -7‰ for Fe-, -2‰ for Mo-nitrogenase), regardless of $N_2$ fixer phylogeny or metabolism.

Thus, a N cycle in which alternative nitrogenases account for a large fraction of $N_2$ fixation provides a straightforward explanation for the extremely low $\delta^{15}N$ of OAE sediments. Low Mo bioavailability combined with high Fe inputs under the euxinic conditions proposed for OAEs may have led to greater reliance on alternative nitrogenases. Results indicate that the role of alternative nitrogenases may have been underestimated in low oxygen/sulfidic environments, and understanding their importance in modern environments is imperative.

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