

## The trace elemental geochemistry in black rock series of early Cambrian from northwestern Hunan, China – An implication for Palaeo-oceanic environments

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### Geological Setting

The Early Cambrian strata is mainly composed of black shales, cherts and mudstones, which distribute along the southeastern margin of Yangtze Platform, South China, forming a black-rock-series belt with a total coverage around 500,000km<sup>2</sup>. Systematical samplings for trace elemental concentrations were taken along the geological profile of Ganziping about 10km NW of Zhangjiajie city.

### Results and discussion

Samples of black shales and cherts collected from the Niutitang Formation of Early Cambrian in Northwestern Hunan Province, China, were analyzed for trace elements and REEs. The determination of trace element and REE concentrations were taken using inductively-coupled plasma mass spectrometry at the State Key Lab for Mineral Deposits Research, Nanjing University. Analytical precisions for the concentrations of trace elements and REEs are better than 5%.

The trace element geochemical characteristics of the ore layer (The high enrichments of Ni, Mo, V, U, Cu, Pb, Zn, Cd, Tl and Ba; The high U/Th ratios and LREE-enriched patterns with positive Eu anomalies and positive Y anomalies) support the assumption that the Ni-Mo polymetallic layer is of submarine hydrothermal origin. High field strength elements (HFSE) and lithophile elements such as Nb, Ta, Zr, Hf, Li, Be, Rb, Cs, Th and Sc are remarkably higher in the upper unit than the lower unit of the Niutitang Formation. These features may reflect that hydrothermal contributions were diminished, terrigenous constituents were increased in the sediments of the upper unit of the Niutitang Formation. The lithostratigraphic change and concentration variations of trace elements in Niutitang Formation that suggest that the black rock series is a regressive succession

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## Investigating nitrogen biosignatures in Early Archean and Proterozoic metasedimentary phyllosilicates

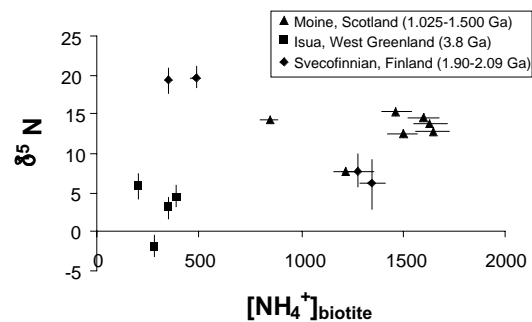
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During sedimentation and diagenesis of organic matter, nitrogen is released as ammonium cation (NH<sub>4</sub><sup>+</sup>) that can then substitute for K<sup>+</sup> in clays (Williams et al., 1995). Such geochemically fixed NH<sub>4</sub><sup>+</sup> potentially preserves the original nitrogen isotopic composition of sedimentary organic matter. The intrinsic thermal stability of substituent NH<sub>4</sub><sup>+</sup> in interlayer sites of K-containing phyllosilicates (e.g. biotite) promotes retention of <sup>15</sup>N/<sup>14</sup>N during metamorphic recrystallization. Isotopic fractionation of <sup>15</sup>N/<sup>14</sup>N and thereby δ<sup>15</sup>N<sub>MICA</sub> derives from devolatilization of structural NH<sub>4</sub><sup>+</sup> (Haendel et al., 1986) and preferential loss of <sup>15</sup>N. μFTIR spectroscopy was used to evaluate the concentration of structural NH<sub>4</sub><sup>+</sup> in mica. Ammonium concentrations >200ppm are considered indicative of a biological origin for the nitrogen (e.g. Boyd, 2001). A calibration was developed for measuring [NH<sub>4</sub><sup>+</sup>]<sub>BIOTITE</sub> directly from μFTIR spectra using absorbance of the N-H stretching (at 1430cm<sup>-1</sup>) and Si-O vibration (at ~1645cm<sup>-1</sup>). Biotites from pelitic schists from Isua, West Greenland (~3.8 Ga), the Svecofennian of Finland (1.90-2.06 Ga) and Moine, Scotland (1.025-1.500 Ga) were then selected for δ<sup>15</sup>N measurements by laser mass spectroscopy.



All investigated samples have [NH<sub>4</sub><sup>+</sup>]<sub>BIOTITE</sub> (>200 ppm) pointing to a biological origin for the nitrogen. Reported δ<sup>15</sup>N represent maximum values of <sup>15</sup>N/<sup>14</sup>N before metamorphic devolatilization. Nitrogen data for the Isua biotites are consistent with phylogenetic evidence for the ancient evolution of biological nitrogen fixation and the δ<sup>15</sup>N values of the Proterozoic biotites are consistent with geochemical evidence from kerogens for an increase in δ<sup>15</sup>N in the Paleoproterozoic due to >pO<sub>2</sub> (Beaumont and Robert, 1999) and the rise of denitrification.