Nitrogen in the sediments of the Onverwacht Group, Barberton Greenstone Belt, South Africa

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Nitrogen is a valuable environmental tracer and a chemical fossil due to its involvement in life metabolisms and its stable behaviour in most crustal processes, preserved as a mineral component in potassium bearing phases (NH4; Boyd,2001). Beaumont and Robert (1999) determined light isotopic ratios for N down to 6.2 permil in organic matter extracted from cherts of various Early Archean greenstone belts. They argued that low N isotopic ratios compared to modern values (from permil,Peters et al.,1978) may be related to a lower oxidation state at the Earth's surface. This implies a microbial consumption of reduced N species in opposition to the present-day cycle of N that is based on nitrification/denitrification processes. However,information provided solely by organic matter may be biased by diagenetic and metamorphic degradation. Pinti et al. (2001) analyzed bulk Archean cherts and BIFs from different localities and identified similar mineral-hosted nitrogen having a light isotopic signature (-6 permil). The issue of a global nitrogen isotopic shift related to the emergence of oxic surface conditions is critical. These low N isotopic ratios were determined in samples related to hydrothermal activity and they could represent the signature of chemiotrophic ecosystems that may not be exclusive on the early Earth (as discussed by Pinti and Hashizume,2001). If Beaumont and Robert's hypothesis is correct,samples unrelated to hydrothermal vents should give similar isotopic signatures. If not,the Archean nitrogen cycle could have been similar to the ongoing one,implying an oxygen rich atmosphere 3.5 billion years ago.The Onverwacht Group in the Barberton Moutain Land,South Africa,is one of the oldest remnants of low-grade metamorphosed supracrustal sequence on Earth,bearing ages of 3.5 Ga. It is made of mafic and silicified felsic volcanics as well as volcanoclastic sediments,minor carbonates and evaporites (Lowe and Knauth,1977). Microfossils from these sediments have been most recently reported by Walsh (1991) and Westall et al. (2001).We analyzed clastic and volcaniclastic cherts from the Onverwacht Group ranging in lithologies from silicified conglomerates to siltstones that are not directly related to hydrothermal vents. Mineralogy,characterized using optical microscopy and SEM,is defined as quartz-sericite-K-feldspar assemblage with minor Ti-oxides,apatite and zircon. Organic matter is apparent as bedding parallel layers in fine grained levels. The matrix of these cherts is a typical association of microcrystalline granular quartz inter-grown with K-micas.Whole rock N isotopic analyses were performed using a quadrupole mass spectrometer after step-wise combustion following the procedure described by Pinti et al. (2001). C contents were determined by pressure measurement. The step-wise procedure allows for separation of organic and mineral N and identification of individual isotopic ratios. Preservation of elemental and isotopic N compositions with the mineral transformation of the ammonium bearing phases is discussed (for example in the K-feldspar to K-mica replacement process). Finally,we provide new insights to the Archean nitrogen cycle issue.

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