

Re-investigating the nitrogen budget in the upper continental crust

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Nitrogen in sediments primarily results from its original sequestration from the atmosphere by biological activity (as opposed e.g. to abiotic processes). After its cycling in ocean, burial, diagenesis, magmatism and/or metamorphism, some nitrogen will ultimately enter the continental crust where it can be stored over geological periods of time. Its amount and isotope composition remain however little constrained.

Upper continental crust N-budget has been estimated by various authors between 40 and 80 ppm NH₄ but all these studies rely on a same data compilation of Wlowska (1972). A value of ~80 ppm NH₄, means that a about 1/5 of atmospheric nitrogen is presently stored in the upper continental crust.

To better address this issue, we have initiated a re-investigation of the nitrogen content and isotope composition of the upper continental crust. Representative loesses and shales previously studied for major and trace elements (although Rb is commonly lacking) were thus considered.

Results illustrate substantial variations in N-contents from ~100 to ~1000 ppm NH₄, yet with little variability in δ¹⁵N-values (5.8 ± 1.2 ‰ vs. AIR, 1σ). The latter suggest that N-isotopes are little affected during processes related to shale formation *sensu lato*. Contrasting with present day sediments and metasediments showing a strong positive correlation between N-contents with potassium and other large ion-lithophile elements, shales display inversely correlated relation with K-, Cs, or Nb/Cs contents.

Instead nitrogen contents show a striking positive correlation with the Chemical Index of Alteration (r² = 0.8), and therefore display positive relationship with e.g. Li-contents, SiO₂/Al₂O₃ and inverse relationship with K/U, etc...

Considering upper continental crust K/U-ratios leads to re-evaluate the budget of nitrogen in this reservoir by a factor from 2.5 to 5, suggesting that large amounts of nitrogen (up to 50%) of early atmosphere is presently stored in the upper continental crust.

[1] Wlowska (1992) Nitrogen. In Handbook of Geochemistry (Wedepohl, Ed.) Springer.

Evidence of sulfur degassing in komatiite-hosted Ni-PGE ores

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The Wannaway komatiite-hosted Ni-PGE sulfide deposit is located in the Archean Ni-rich Kambalda Domain, Yilgarn Craton, Western Australia. This typical Type 1 orebody occurs at the base of a komatiite flow overlying sulfide-rich black shales and metabasalts and is characterized by a pyrrhotite-pentlandite assemblage with minor chalcopyrite and PGE-bearing Ni-Co sulfosalts. Detailed petrographic and mineralogical studies of a drillcore across the mineralized sequence were the basis for ion probe multiple S isotope analyses on pyrrhotite and pentlandite in basal massive to matrix/disseminated ore facies, and in black shales. Plots of δ³⁴S vs. Δ³³S can separate the effects of mass-dependent fractionation (δ³⁴S variability without Δ³³S variability) from mass-independent fractionation (Δ³³S variability). Non-zero values of Δ³³S fingerprint crustal S reservoirs in the Archean, characterized by intense photochemical reactions between S-bearing gases and unshielded solar UV rays [1]. In the δ³⁴S-Δ³³S diagram, both komatiite-hosted ore and black shale samples plot at positive non-zero values of Δ³³S, compatible with sulfur saturation of magma via assimilation of S-rich sediments. However, ore and black shales show different δ³⁴S-Δ³³S patterns. Black shales possess remarkable dispersion in Δ³³S, in contrast to the flat Δ³³S arrays for both ore-related pyrrhotite and pentlandite, which are in textural, chemical and isotopic equilibrium. Ore data for both phases display shifts in δ³⁴S values related to stratigraphy and sulfide mineralogy, and testify to progressive lowering of δ³⁴S signatures from basal massive ore upwards. Such a trend may correlate with intense isotopically heavy SO₂ outgassing of the lava [2], as proposed for similar isotopic imprints observed in other komatiite-hosted ores [3].

[1] Jamieson *et al.* (2006), *Econ. Geol.*, **101**, 1055-1061. [2] Marini *et al.* (2011), *Rev. Min. Geoch.*, **73**, 423-492. [3] Isaac *et al.* (2012), I.G.C., Brisbane, 5-10th August 2012.