Nitrogen behavior during fluid-rock interactions in a continental subduction zone: Results from the Dora-Maira Massif whiteschists

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Earth's atmosphere hosts around 30% of the nitrogen (N) on Earth and plays a major role in biogeochemical processes. Yet, estimates show that the deep Earth holds the majority of Earth's N budget (~50–60% in the mantle and ~11–16% in the crust). The role of geological N has been understudied and little is known about the N behavior during fluid-rock interactions at mantle depths in the subduction pathway. Based on mineralogy, fluid inclusions, major and trace element geochemistry, and other stable isotope compositions (O, Mg, Li, B, and Fe; see Chen *et al.*, 2019; Xiong *et al.*, 2022), the Dora Maira ultrahigh-pressure whiteschists (Italian Alps) are presumed to have been formed from the interaction of serpentinite-derived fluids with a metagranite protolith (country rocks). Thus, they represent an opportunity to study N behavior during fluid-rock interactions in a continental subduction zone.

Analyses of N in whole-rock samples (same as in Chen *et al.*, 2016) previously analyzed for other isotope tracers, on the average, show a decrease in concentration and increase in $\delta^{15}N$ relative to their presumed protoliths. The whiteschists contain 16.4 ± 2.4 ppm N with $\delta^{15}N_{air}$ = +4.2 ± 0.7‰, while the metagranites contain 34 ± 4.0 ppm N with $\delta^{15}N$ = +0.3 ± 1.4‰ (Fig. 1). The loss of N was accompanied by loss of LILE (Rb, K, Ba), Na, Ca, Sr, and Fe. Among the LILE, Rb shows greater correlation with N than K or Ba. Although the whiteschists show minor differences in $\delta^{26}Mg$, $\delta^{7}Li$, $\delta^{18}O$, and $\delta^{56}Fe$ from their protoliths, these isotope shifts do not obviously correlate with any shift in $\delta^{15}N$. The infiltration and interaction of a serpentinite-derived fluid depleted in N and LILE with the metagranite could have leached N and produced a positive isotope shift by a process resembling Rayleigh distillation, assuming three possible starting N and $\delta^{15}N$ compositions for the protolith. A fluid from that source and composition is consistent with typical N concentrations and $\delta^{15}N$ of serpentinite. The N exchange and leaching process is best explained as involving N_2-NH_4 and NH_3-NH_4 at 560-590°C, the latter the approximate temperature at which the fluid infiltration is assumed to have taken place. These results provide new insights regarding N behavior and isotopic fractionation during fluid-rock interactions occurring in UHP rocks in continental subduction zones.

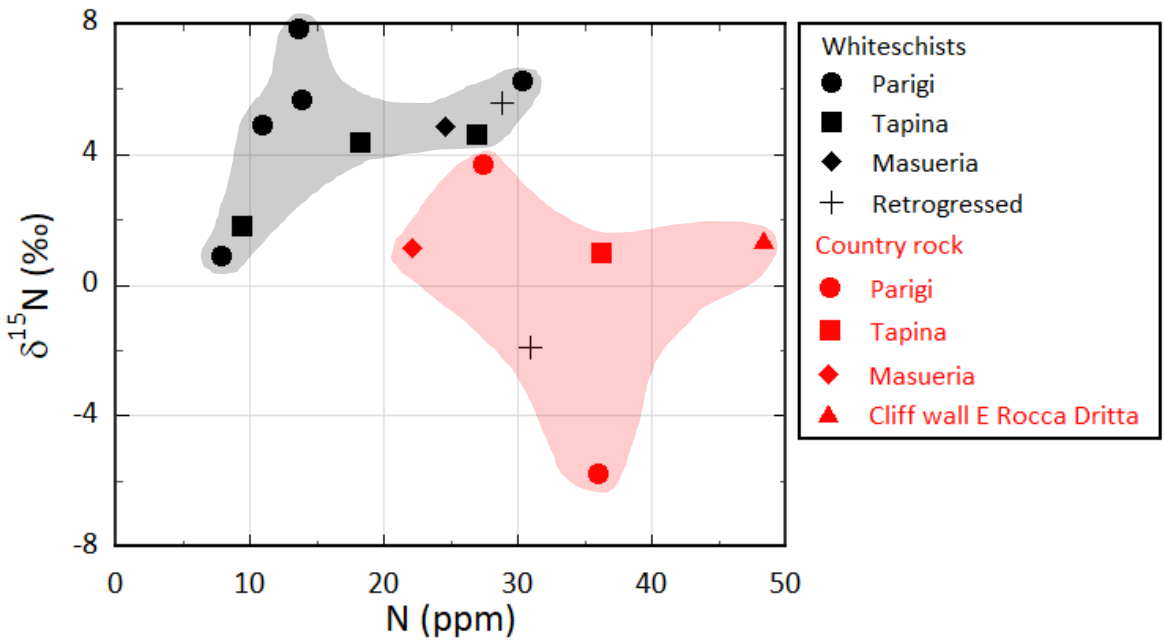

Figure 1- The N concentrations vs. $\delta^{15}N_{air}$ values for the Dora Maira whiteschists and country rocks. The localities and number of whiteschists and metagranites (country rock) samples are the same as in (Chen et al., 2016, 2019).

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Chen, Y. X., Lu, W., He, Y., Schertl, H. P., Zheng, Y. F., Xiong, J. W., & Zhou, K. (2019). Tracking Fe mobility and Fe speciation in subduction zone fluids at the slab-mantle interface in a subduction channel: A tale of whiteschist from the Western Alps. *Geochimica et Cosmochimica Acta* 267, 1-16.

Xiong, J.-W., Chen, Y.-X., Ma, H.-Z., Schertl, H.-P., Zheng, Y.-F. and Zhao, K.-D. (2022) Tourmaline boron isotopes trace metasomatism by serpentinite-derived fluid in continental subduction zone. *Geochimica et Cosmochimica Acta* 320, 122-142.