Hydrothermal recycling of sedimentary ammonium into oceanic crust and the Archean ocean at 3.24 Ga

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Abstract

The Archean ocean supported a diverse microbial ecosystem, yet studies suggest that seawater was largely depleted in many essential nutrients, including fixed nitrogen (N). This depletion was in part a consequence of inefficient nutrient recycling under anoxic conditions. Here we show how hydrothermal fluids acted as a recycling mechanism for ammonium (NH_4^+) in the Archean ocean. We present elemental and stable isotope data for C, N, and S from shales and hydrothermally altered volcanic rocks from the 3.24 Ga Panorama District in Western Australia. This suite documents the transfer of NH_4^+ from organic-rich sedimentary rocks into underlying sericitized dacite, similar to what is seen in hydrothermal systems today. On the modern Earth, hydrothermal fluids that circulate through sediment packages are enriched in NH_4^+ to millimolar concentrations because they efficiently recycle organic-bound N. Our data show that a similar hydrothermal recycling processes dates back to at least 3.24 Ga, and may have resulted in localized centres of enhanced biological productivity around hydrothermal vents. Lastly, our data provide evidence that altered oceanic crust at 3.24 Ga was enriched in N and, when subducted, satisfies the elemental and isotopic source requirements for low N, but ^{15}N-enriched, deep mantle N reservoir as sampled by mantle plumes.

Introduction

Early life on Earth thrived in an anoxic ocean where the supply of key nutrients was likely suppressed (Lyons *et al.*, 2014). High rates of biomass burial on the seafloor due to scarcity of oxidants limited the recycling of organic-bound nutrients, which on the modern Earth is a major driver of biological productivity (Kipp and Stüeken, 2017; Kipp *et al.*, 2021). Nevertheless, we have a notable record of life from the Archean eon (Buick, 2007), which opens the question of how biological productivity could be sustained under such nutrient-limited conditions? Trace element data indicate that the Archean ocean saw enhanced levels of hydrothermal activity (Viehmann *et al.*, 2015). Hydrothermal circulation could therefore have played an important role in replenishing marine nutrient supplies. Today, hydrothermal metal fluxes are dispersed widely

across the ocean (Ardyna *et al.*, 2019), and Precambrian banded iron formations indicate that a similar dispersal occurred throughout Earth's history (Isley and Abbott, 1999). Further, there is evidence from modern black smokers that hydrothermal fluids are able to recycle sedimentary NH_4^+ back into the water column (Lilley *et al.*, 1993). However, it is unknown if hydrothermal circulation affected the availability of N in the Archean and if it could have mitigated the absence of respiratory biomass recycling that dominates the ocean's nutrient budget today (Kipp and Stüeken, 2017). To address this question, we investigated N, organic C and S geochemistry in the 3.24 Ga Panorama district in Western Australia. This area contains the oldest known volcanogenic massive sulfide deposit (VMS) (Vearncombe *et al.*, 1995) and offers an opportunity to study hydrothermal N cycling in the Archean.

Geological Setting

The Panorama district on the East Pilbara craton in Western Australia comprises three geologic units (Fig. 1): (i) The Sulphur Springs Group, 3235-3238 Ma (Buick *et al.*, 2002), is composed of a 2 km-thick sequence of volcanic rocks ranging from tholeiites at the base to dacites/andesites at the top. Rhyolite domes occur locally. Absence of explosive textures, and presence of pillow lavas, are interpreted as evidence for deep marine eruption below ca.1000 m (Vearncombe *et al.*, 1995). The volcanic pile is capped by a 20 m-thick bed of silicified sediments, called the marker chert. VMS mineralisation is localised within the dacites and the marker chert horizon (Vearncombe *et al.*, 1995). (ii) The Strelley granite intruded the Sulphur Springs Group in two phases, at 3239 ± 2 and 3238 ± 3 Ma (U-Pb zircon age), *i.e.* indistinguishable from the eruption of the extrusive volcanic rocks (Buick *et al.*, 2002). The intrusion of granitoids likely acted as a heat source for hydrothermal circulation within the Sulphur Springs Group (Brauhart *et al.*, 1998). Granophyres occur at the upper contact of the granitoids. (iii) The Soanesville Group turbidites unconformably overlay the Sulphur Springs Group and reach over 1.6 km in thickness (Van Kranendonk *et al.*, 2006). Reworking of solidified marker chert rip-ups indicates a depositional hiatus between the Sulphur Springs Group and the Soanesville Group; however, the similarity in regional peak metamorphic grade (prehnite-pumpellyite facies, Brauhart *et al.*, 1998) and in deformation suggest that the age difference is small (Buick *et al.*, 2002). Cross-cutting mafic sills dated at 3200 Ma provides a minimum age for the Soanesville Group (Van Kranendonk, 2002).

The entire succession is tilted by 50-60°, such that subsequent erosion has exposed a cross section of the paleo-seafloor (Brauhart *et al.*, 1998). Relics of massive sulfide deposits occur at roughly 5-7 km spacing. Measurements of alteration minerals and oxygen isotopes have revealed that these intervals correspond to hydrothermal convection cells, consisting of recharge and discharge zones (Brauhart *et al.*, 1998; Brauhart *et al.*, 2000; van Ruitenbeek *et al.*, 2012). The recharge zone closer to the seafloor shows enrichment in K associated with sericite alteration; deeper parts of the volcanic pile and the hotter discharge zone are characterized by (plagioclase-)quartz-chlorite alteration (Brauhart *et al.*, 1998; Brauhart *et al.*, 2001). We selected 39 drill core samples from core VSD007 (21.1768° S, 119.2278° E), supplemented by 14 outcrop samples (Table A1). The drill core intersects turbidites from the Soanesville Group, the marker chert and the upper portion of sericitized dacite in the Sulphur Springs Group in a hydrothermal recharge zone. The outcrop samples capture quartz-chlorite ($\pm$ plagioclase) alteration zones of basaltic-andesitic volcanic rocks as well as the granophyre intrusion at the base of the volcanic pile. These samples were decarbonated and analysed for organic C, total N and total S content and isotopic composition with an EA-IRMS, following standard protocols (Appendix A1). For N-poor samples,

the abundance and stable N isotope values were verified with a second method employing offline sealed-tube combustion (Boocock *et al.*, 2020) (Appendix A2). Where both methods were used, $\delta^{15}N$ data agree to within 1.0 ‰ on average; TN abundances agree to within 20% and show identical trends (Figure A1). For consistency, the discussion is based mostly on the EA dataset; the sealed-tube combustion data are used where we were unable to obtain EA data (see Table A2). Major and minor element data for a subset of core samples were obtained from the Geological Survey of Western Australia. Outcrop samples were sent to Australian Laboratory Services in Dublin for major element analyses by ICP-MS (Appendix A3).

Results

From the shales to the chert in core VSD007, total organic carbon (TOC) decreases by a factor of 17 from 4900 ± 1900 µg/g to 298 ± 198 µg/g (with one outlier of 1780 µg/g) (Fig. 2). Similarly, total nitrogen (TN) decreases by a factor of 16 from 91 ± 25 µg/g to 6 ± 6 µg/g (with one outlier of 54 µg/g). Between the chert and the sericitized dacite, TOC decreases by another factor 9 down to 20 ± 13 µg/g whereas TN roughly doubles relative to the chert to 15 ± 6 µg/g. TN concentrations in the sericitized dacite thus exceed those of the deeper volcanic pile and granophyre (around 4 ± 1 µg/g with slightly higher values of 8-14 µg/g towards the top). The low N concentrations found in these deeper parts of the Archean seafloor are comparable to those of unaltered oceanic basalts elsewhere (1.4 ± 1.3 ug/g, Johnson and Goldblatt, 2015). The sericitized dacite is clearly enriched in nitrogen down to at least 280 m and possible up to 650 m (Fig. 2, 3c), independent from TOC (Fig. 3a), with similar N concentrations to altered Phanerozoic oceanic basalts (Busigny et al., 2019). The observed difference between the sericite zone and the combined granophyre and quartz-chlorite discharge samples, which are furthest away from the recharge area and probably reflect magmatic background, is statistically highly significant ($p < 10^{-5}$). Across the chert and altered dacite, K/Al ratios plot close to those of muscovite, interpreted to reflect sericitization (Fig. 3d). Quartz-chlorite(-plagioclase) phases define a different trend, reflecting scarcity of sericite in these rocks.

$\delta^{15}N$ values decrease slightly across the same interval from +1.5 ± 0.7 ‰ in the shales and +0.8 ± 1.7 ‰ in the chert to +0.1 ± 1.2 ‰ in the altered dacite and -3.6 ± 0.6 ‰ in the deeper volcanic pile (Fig. 2). The shale data agree with previous measurements of the unaltered Soanesville Group (Stüeken *et al.*, 2015b) while the data from the deeper volcanic rocks are comparable to the mean mantle $\delta^{15}N$ of -5 ± 3 ‰ (Cartigny and Marty, 2013). Total sulfur (TS) is heterogeneous across the section, driven by local enrichments of secondary sulfides. Broadly speaking, abundances are higher in the altered dacite and chert (1600 ± 2600 µg/g) than in the shales (700 ± 400 µg/g). C/S ratios are therefore highest in the shales (Fig. 2) with a slight increase from ca. 10 to 40 up section. Previous measurements of the upper, more distal Soanesville Group shows C/S ratios tightly clustered around a mean of 33 ± 7 (n = 9) (Stüeken *et al.*, 2015a). Most samples analysed in this study fall below this value (Fig. 3b). $\delta^{34}S$ values are relatively uniform throughout the section with a mean value of +2.0 ± 1.3 ‰, similar to previous data from distal Soanesville shales +1.1 ± 0.9 ‰ (Stüeken *et al.*, 2015a) and reflecting a largely volcanic origin.

Discussion

Hydrothermal ammonium mobilization

Sericitization of the dacite (Fig. 3d), silicification of the lowermost sedimentary unit (the marker chert) and enrichment in S throughout most of the drill core reflect extensive hydrothermal fluid flow through this sequence shortly after emplacement at 3.24 Ga (Huston *et al.*, 2001; Johnson and Wing, 2020). Hydrothermal circulation has altered at least the lowermost 20-50 m of the Soanesville Group in this area, based on the relatively low C/S ratios compared to background values in distal parts of the Soanesville Gp (Stüeken *et al.*, 2015a). Oil inclusions in hydrothermal barite deposits in the Sulphur Springs Gp have been interpreted as evidence of hydrothermal alteration of organic matter based on the isotopic similarity in $\delta^{13}C$ to the organic-rich shales of the Soanesville Gp (Rasmussen and Buick, 2000). Hence, there is extensive evidence for hydrothermal fluid circulation through both the volcanic and sedimentary packages.

The interaction between organic matter and hot fluids alters organic amines into aromatic rings permitting the mobilisation of NH_4^+ (Ader *et al.*, 2006; Boudou *et al.*, 2008). NH_4^+ can migrate away from source rocks (Koehler *et al.*, 2019), and due to the +1 charge and similar radius to Rb^+ and K^+, NH_4^+ can be incorporated into potassic phyllosilicate phases (e.g., Schroeder and McLain, 1998). In the case of Sulphur Springs, the sericite in the upper few hundred meters of the volcanic pile (Brauhart *et al.*, 1998; van Ruitenbeek *et al.*, 2012) provides the most likely mineral host for liberated NH_4^+ sourced from the organic-rich shales in the Soanesville Gp. We note that N and K are not correlated in the sericite zone ($r^2 = 0.001$, Figure 3c); however, if the NH_4^+ was derived from organic-rich sediments, it likely postdates the onset of sericitization, which has been linked to downwelling of K-bearing seawater and probably started before sediment deposition (Brauhart *et al.*, 2001). Correlation between N and K abundances is therefore not expected. Importantly, our data reflect hydrothermal transport of NH_4^+ from organic-rich sediments into the upper oceanic crust, independently from organic C as evidenced by the very low C/N ratios of the altered oceanic crust (Fig. 2). Hydrothermal mobilization of organic N does not impart a significant isotopic fractionation (Boudou *et al.*, 2008), consistent with the close isotopic match between the Soanesville shales and the Sulphur Springs sericitized dacite. In contrast, the deeper parts of the Sulphur Springs Gp and the intrusive granophyre show $\delta^{15}N$ data that are isotopically indistinguishable to Earth's mantle (Cartigny and Marty, 2013). These samples may thus reflect the presence of primary magmatic N that has not been overprinted by hydrothermally-sourced NH_4^+. If so, then hydrothermal N enrichment appears to be present in at least the upper 100 m of the Archean seafloor, where the $\delta^{15}N$ values are several permil heavier than the mantle value. This conclusion matches observations from the modern Pacific ocean, where hydrothermal fluids have enriched the upper 150 m of oceanic crust in N to ca. 20 $\mu g/g$ (Li *et al.*, 2007).

Hydrothermal ammonium recycling

Today, hydrothermal vent fluids that are discharged from the modern seafloor are enriched in NH_4^+ up to 20 mM concentration if the vent site is associated with a sedimentary cover (Von Damm *et al.*, 1985; Lilley *et al.*, 1993). This concentration is 2-3 orders of magnitude greater than background levels of fixed N in the open ocean and in anoxic marine basins such as the Black Sea (Brewer and Murray, 1973). Hydrothermal convection is therefore evidently more efficient in mobilising NH_4^+ from organic matter than diffusive processes from sediments alone. While NH_4^+ can build up to high concentrations in sedimentary pore-waters and support diverse ecosystems locally (D'Hondt *et al.*, 2004), vents can disperse nutrients over hundreds of kilometers and into the photic zone (Ardyna *et al.*, 2019), making them basin-scale nutrient sources. Based on our data, we postulate that hydrothermal NH_4^+ recycling operated already during the Archean. Hydrothermal vents of the Sulphur Springs Gp thus likely discharged NH_4^+ in the Archean ocean

(Fig. 4), recycled from the lower Soanesville sedimentary package. This is consistent with previous work which links the hydrothermal expulsion of oil and pyrobitumen in discharge zones of the Sulphur Springs Gp to the Soanesville shales (Rasmussen and Buick, 2000). Microfossils associated with the ore deposit indicate that these vents were inhabited (Rasmussen, 2000), and therefore it is conceivable that these organisms were taking advantage of local nutrient supplies from the vent. Hence these vent sites may have created basin-scale hotspots of biological productivity in an anoxic world where nutrient recycling by respiration was otherwise suppressed (Kipp and Stüeken, 2017).

The source of ^{15}N-enrichment in mantle-derived samples?

Lastly, our data provide an Archean example for N transfer from organic matter into oceanic crust, which has implications for interpreting the record of N in mantle-derived igneous rocks. Previous studies documented N with sediment-like $\delta^{15}N$ values (range from -2 to +8 ‰, Cartigny and Marty, 2013) in mantle plume-derived ocean island basalts (OIB) and carbonatites from the Kola peninsula (Russia). A difficulty in explaining these data has been the low abundance of N in these rocks (< 2 μg/g), which is orders of magnitudes lower than in sedimentary source rocks (560 ± 230 μg/g) (Johnson and Goldblatt, 2015). A potential mechanism for transferring trace amounts of sedimentary N into the mantle is hydrothermal enrichment of oceanic crust, followed by subduction. This model has been posited for the Phanerozoic (Halama *et al.*, 2014; Busigny *et al.*, 2019), and our data from the Panorama District reveal that during the Archean transfer of NH_4^+ from sediments into altered oceanic crust was significant and perhaps similar in magnitude to the modern. The subduction of hydrothermally altered igneous oceanic crust in the Archean is therefore a feasible mechanism for generating N-depleted but ^{15}N-enriched mantle domains in the Archean mantle.

Conclusions

Our data reveal that hydrothermal N cycling dates back to at least 3.24 Ga. Similar to today, hydrothermal fluids in the Archean were able to mobilise NH_4^+ from organic-rich sediments. However, unlike today, this recycling mechanism of fixed N may have represented an important basin-scale nutrient source in an otherwise nutrient-starved world. Furthermore, our data provide evidence that small amounts of sedimentary NH_4^+ were trapped in altered oceanic crust and may have constituted a relatively N-poor source flux with sedimentary $\delta^{15}N$ signatures into Earth's mantle over the past few billion years.
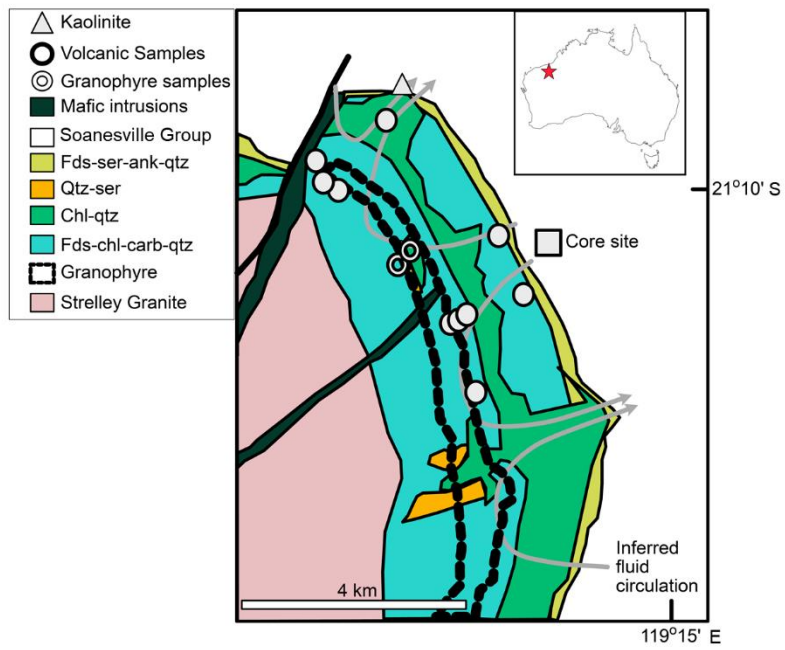
Figures

Figure 1: Map of the Panorama District with sampling sites and inferred hydrothermal circulation.
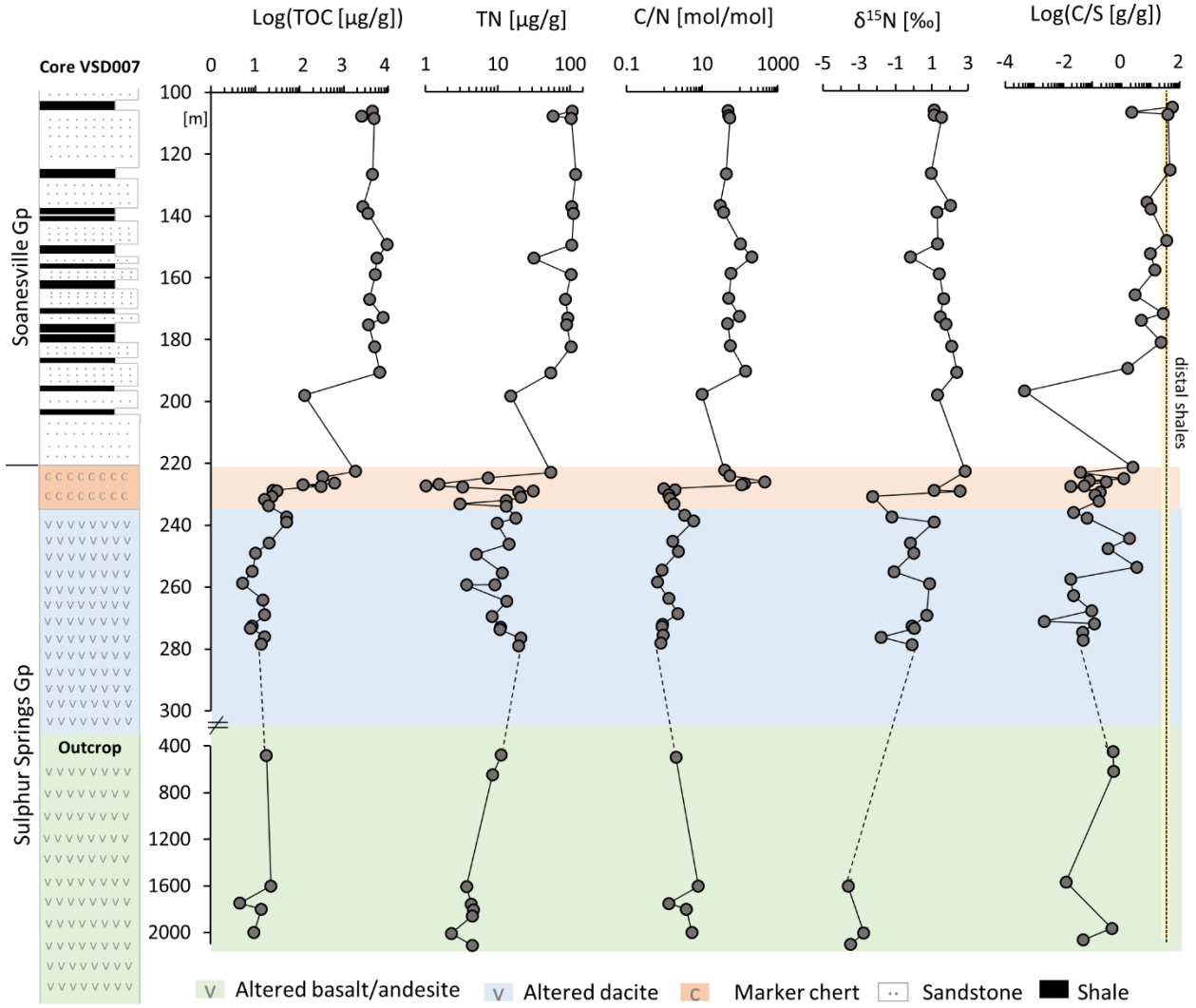
Figure 2: Recharge zone profiles. 100-280m = core VSD007, 400-2100m = outcrop. Error bars are mostly smaller than symbols.
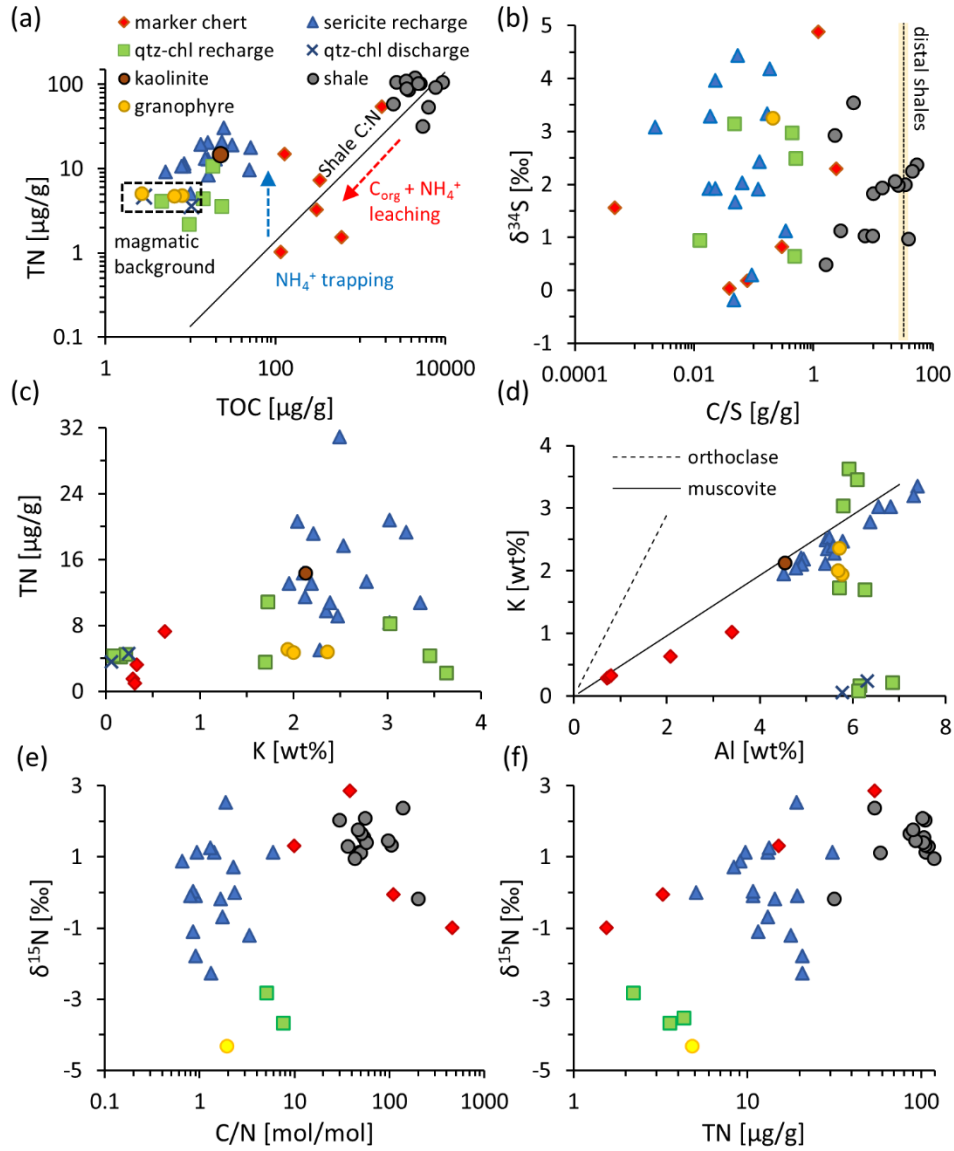
Figure 3: (a) TN vs. TOC. (b) $\delta^{34}S$ vs organic C to total S ratios. Distal shale data from Stüeken *et al.* (2015a). (c) Total N vs. K, excluding one chert point at 54 µg/g N and 1.02 wt.% K. (d) K vs. Al. (e) $\delta^{15}N$ versus C/N ratios. (f) $\delta^{15}N$ versus TN abundances.
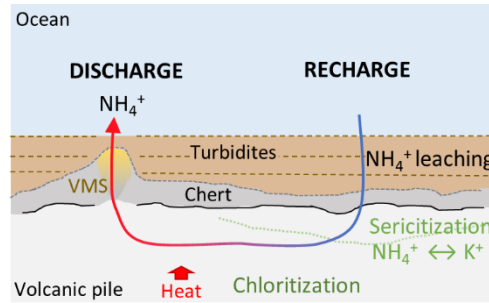
Figure 4: Schematic of hydrothermal NH_4^+ transport. NH_4^+ is mobilised from lower Soanesville sediments. Some NH_4^+ is trapped in sericitized volcanic rocks. Deeper chloritized rocks are N-poor. As in modern vents, significant NH_4^+ is discharged into the ocean.

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