

## Precambrian nickel sources and sinks

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The trace element database for BIF shows a trend in Ni/Fe ratios that can be defined by two broad stages. Stage 1, from ca 3.8 to 2.7 Ga, shows a uniform maximum molar Ni/Fe ratio ( $\sim 4.5 \times 10^{-4}$ ). Stage 2, which begins ca. 2.5 Ga, shows strikingly lower maximal Ni/Fe ratios (below  $2.2 \times 10^{-4}$ ). The boundary between stages 1 and 2, although presently not well constrained due to gaps in the BIF record, marks a significant and irreversible decline in oceanic Ni concentrations: stage 1 values are never reached again. Stage 2 is characterized by a further steady decline in maximum Ni/Fe ratios, a trend that persists for the remainder of the Paleoproterozoic BIF record. It is possible that a third stage exists, post-dating a resurgence in BIF deposition between 0.75 and 0.55 Ga, but the scarcity of Neoproterozoic BIF trace element data precludes any further conclusion at this time.

The transition from stage 1 to stage 2 is unlikely to have been driven by changes in Ni sinks, which appear to be relatively insensitive to evolving major element and redox conditions from Archean-Paleoproterozoic ferrous iron seas, through Mesoproterozoic sulfidic seas, to the onset of oxygenated bottom waters in the Neoproterozoic.

In contrast, Ni supply likely changed significantly with time. First, a hotter Archean mantle produced abundant Ni-rich komatiite and olivine-rich basalt in oceanic crust, plateaus, and perhaps on land. Second, Archean tholeiites, which made up most of the oceanic crust, were richer in Ni than their modern counterparts. Third, a major peak in preserved komatiite abundance occurred during the most intense period of mantle plume magmatism and continental crustal growth in Earth's history, between 2.72 and 2.66 Ga, after which their abundance decreased rapidly. Hence, the hotter Archean mantle produced more Ni-rich ultramafic rocks, resulting in a much greater supply of Ni than any time thereafter, a fact reflected in the similarity between the lava eruption temperature vs. age curve and the molar Ni/Fe ratio of BIF.

## Greater average chain length of *n*-alkanes correlates with D-depletion and <sup>13</sup>C-enrichment in evergreen angiosperms in comparison with other higher plant species

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Several recent studies indicate that coexisting higher plants with the same biosynthetic pathways but contrasting physiology may have significantly different D/H and <sup>13</sup>C/<sup>12</sup>C compositions. Because the extent of these differences is of the same magnitude as the  $\delta D/\delta^{13}C$  excursions displayed by sedimentary biomarkers, these findings deserve attention from palaeoclimatologists who need to find a reliable method for identifying shifts in the contribution of isotopically different plant species during periods of climate change.

In order to identify such a method, we investigated  $\delta D/\delta^{13}C$  and average chain length (ACL) of leaf wax *n*-alkanes in angiosperms and conifers in Newcastle, UK. The *n*-C<sub>29</sub> alkane data from 12 species show a negative trend between  $\delta^{13}C$  and  $\delta D$ . The evergreen angiosperms ( $\delta D$  -193 to -164‰;  $\delta^{13}C$  -32.7 to -28.4‰) are clearly separated from the deciduous angiosperms ( $\delta D$  -153 to -130‰;  $\delta^{13}C$  -39.5 to -34.8‰), while the conifers ( $\delta D$  -163 to -147‰,  $\delta^{13}C$  -31.9 to 30.6‰) are in the middle. The ACL of the evergreen angiosperms (31.0-31.7) are greater than those of deciduous angiosperms (26.7-30.1) and conifers (27.4-28.0).

Previous studies suggested that the differences in  $\delta D/\delta^{13}C$  of various coexisting plant types could be explained by variations in stomatal conductance to H<sub>2</sub>O and CO<sub>2</sub>, so that species with lower conductances (in our case, evergreen angiosperms) would have D-depleted and <sup>13</sup>C-enriched values. Because a larger proportion of longer chain *n*-alkanes would lead to a more rigid leaf wax structure, greater occlusion of stomata, and reduced gas exchange, our findings that greater ACL in evergreen angiosperms are associated with D-depleted and <sup>13</sup>C-enriched *n*-alkanes provide further support for this explanation. Furthermore, this association between  $\delta D/\delta^{13}C$  and molecular characteristics of biomarkers in modern plants suggests a means for tracing the contribution of isotopically different plants in the past.