General idea

Despite Ni’s biogeochemical importance, we have a poor understanding of its marine cycling, even in the modern oceans. In 1976, Krishnaswami (Krishnaswami, 1976), identified a massive Ni mass imbalance. In the several decades that have followed, we have yet to resolve the imbalance. Currently, our best estimates indicate that Ni sink fluxes from the ocean are twice the size of source fluxes (Ciscato et al., 2018; Gall et al., 2013; Sclater et al., 1976). If this were true, the ocean would be rapidly depleted in Ni, but there is no evidence for such deviation from steady. Once the modern marine Ni budget is balanced, we will have identified the key modern controls of marine Ni cycling and this will enable robust modelling of the marine Ni cycle, and the subsequent affects, over time.

**Inputs**

The primary sources, which total 3.68 x 108 to 1.63 x 109 Ni mol/yr, Ni appear to be dust and rivers (with a potential significant contribution from a benthic flux discussed later) (Ciscato et al., 2018; Gall et al., 2013; Little et al., 2020). Dust is estimated to contribute 2% to 28% of the total marine Ni flux. Rivers are the main contributor of Ni to the oceans and make up an estimated 32% to 97% of the total marine Ni flux. Other suggested sources include riverine particulate matter and a benthic flux from Mn oxide diagenesis. How much Ni is retained in the particulate load versus the dissolved load and how much the particulate load could be mobilized remains unclear. A recent study suggests a significant benthic source from Mn oxide redox cycling and/or diagenetic processes is of the appropriate size to resolve the imbalance (0.6 to 2.3 x 108 mol/yr) (Little et al., 2020). However, their calculations rely on size of this flux and the exact mechanisms at play remain unclear and require further exploration (see section XXX for further discussion).

**Outputs**

Once Ni enters the ocean, its fate is a little less clear. Previous studies have focused on Fe-Mn deposits, organic rich matter, and euxinic sediments. Fe-Mn deposits are typically believed to represent the most significant sink; they compromise between 16% to 73% of the total estimated Ni sink (Ciscato et al., 2018; Gall et al., 2013; Little et al., 2020). Organic rich matter is estimated to be the next most significant sink and make up 23 to 34% of the total estimated Ni sink (Ciscato et al., 2018; Little et al., 2020). Euxinic sediments appear to be a much smaller constituent of the total Ni sink, around 2.5% (Ciscato et al., 2018; Vance et al., 2016), although the significance of sulfidization in organic matter has not been assessed. Some believe that carbonates are an insignificant sink (similar in size to euxinic sediments) (Ciscato et al., 2018; Little et al., 2020), but a recent study argues the ubiquity of carbonate deposition causes the carbonate Ni sink to be as sizeable as the riverine input (1.5 to 6.7 x 108 Ni mol/yr) (Alvarez study 2021).

**Resolving the imbalance**

There are two potential causes of the imbalance (1) missing fluxes or (2) inaccurate flux estimates, or both. Concerning cause 1, obtaining better estimates is a challenging task. However, assuming the ocean is at or near steady state with respect to Ni, the fluxes and the abundance weighted isotopic compositions of the Ni sources and sinks should balance. Therefore, we can use isotope mass balance to constrain the fluxes and Ni marine budget in three dimensions (*i.e.,* mass flux, Ni concentration, and δ60/58Ni, where δ60/58Nisample = (60/58Nisample/60/58Nistandard -1) x 1000‰). To apply this approach, we must know the isotopic compositions of major fluxes. While the isotopic compositions of known sources are reasonably well characterized, the sinks, which are dependent on the isotopic composition of seawater and the sink’s isotope fractionation (Δ60/58Nisolution-output = δ60/58Nisolution - δ60/58Nisink), are difficult to ascertain. Once the major isotope parameters have been identified, we can apply the isotope mass balance constraint, evaluate the flux estimates, and hopefully resolve the mass imbalance.