A chromium isotope record of low oxygen in the Mesoproterozoic

Introduction: The timing of when complex life diversified on Earth was either the result of environmental factors or a biotic trigger. More specifically, fierce debate has surrounded the question of whether the rise of animals is directly linked to change in environmental oxygen levels or if this dramatic shift in structure and complexity of the biosphere simply reflects timing of genetic innovation. The lack of environmental data on Proterozoic environmental oxygen levels, especially just prior to the diversification of metazoans (0.8 - 0.7 Ga) prevents a clear resolution (1). To tackle this problem, I have used the novel chromium isotope system to investigate oxygenation prior to this critical interval. Cr isotopes are capable of providing new constraints on oxygen levels, as significant fractionation is predominantly tied to Cr oxidation in terrestrial settings, and Cr redox cycling occurs at an oxygen threshold below what animals need to thrive (2). By refining our understanding of global oxidative cycling at the end of the Mesoproterozoic, I have shed new light on causative links between oxygenation and the evolution of animal life, a central component of the NASA Astrobiology Roadmap goals.

Background: Estimates for Mid-Proterozoic atmospheric oxygen range from 40% of present atmospheric levels (PAL) based on inferred ocean anoxia and steady-state ocean ventilation models, to < 0.1% PAL based on Cr isotopes from the sparse ironstone record (3, 4). Oxygen levels directly impact the ability of metazoans to survive and diversify due to minimum requirements based on physiology (5). Should new Cr isotope data support extremely low oxygen levels at the end of the Mesoproterozoic, the window of favorable environmental conditions prior to the diversification of metazoans would be quite narrow. This result would have significant implications for the relationship between the origins of diverse animal life and environmental controls.

A record of Cr cycling is preserved in shale, where significant authigenic Cr enrichments can develop. Recent work in the Cariaco Basin has shown that these Cr isotope values act as a reliable recorder of North Atlantic bottom water Cr isotope values at the time of deposition (6). Due to extremely rapid and quantitative consumption of Cr in reducing environments, Cr fractionation in ambient seawater is preserved in the shale record. The absence of fractionation based on comparison with igneous values is indicative of a lack of terrestrial oxidative cycling in the atmosphere, and atmospheric oxygen levels below ~0.1% PAL (Reinhard et al., 2014; Planavksy et al., 2014). The early Neoproterozoic Simla Group, an anoxic shale of Northern India, provides an ideal setting for this study. In addition, we sampled the early Cambrian Tal Group, also exposed in the same region, which can aid in providing a baseline of the type of Cr variability we would be likely to observed in an environment that would have had active oxidative Cr cycling.

Field Localities, Formations and Methods

The focus of this study was on a sequence of early Neoproterozoic to Cambrian sedimentary formations that comprise the outer lesser Himalayan thrust sheet, exposed in Northern India in the states of Himachal Pradesh and Uttarakhand (Fig. 1a). We specifically targeted organic rich black shales that were deposited under reducing conditions – sediments that would have the potential to capture an authigenic Cr signal during deposition. These formations were sampled in road and river cuts with the goal of targeting the most freshly exposed and well-preserved surfaces.

The ~ 0.84 Simla Group

The Simla Group has provided a Re-Os age of 839 ± 139 (7). The Simla is comprised primarily of siltstones and shales with some more organic-rich intervals. Interbedded sandstones are also present. Our sampling was focused on the most organic-rich intervals, which have the best potential for significant Cr enrichments. Our samples were collected at four localities; the first in the Yamuna River valley at N 30.534306°, E 77.906611°, the second on the Simla – Kanga road just north of Bagha at N 31.188918°, E 76.988983°, the third in the Tons river valley just north of Killor at N 30°561624, E 77°.817923, and the fourth on the road between Theog and Matiana beginning at the trash dump at N 31.070550°, E 77.223405°.

The 0.55 Tal Group, Northern India

The Tal Group is exposed in a number of northwest striking synclines in the Krol belt of the Lesser Himalaya region of northwestern India. Based on detailed biostratigraphy precise constraints have been placed on the age, placing the lower black shale member (from which our samples were taken) in the earliest Cambrian Meishucunian stage (8). Additionally, two coherent Re-Os isochrons for the underlying Krol-Tal (Precambrian-Cambrian) boundary have been reported – 554 ± 16 Ma and 552 ± 22 Ma – indicating minimal mobilization of metals during any post depositional alteration (7). The samples of the lower black shale member of the Tal used in this study were collected on the east bank of the Ganges in the town of Kaudiyala on the Haridwar Rishikesh Badrinath road at N 30.073206°, E 78.501584° (Fig. 1b, 1c). The section was freshly exposed due to recent flooding, providing unweathered surfaces.

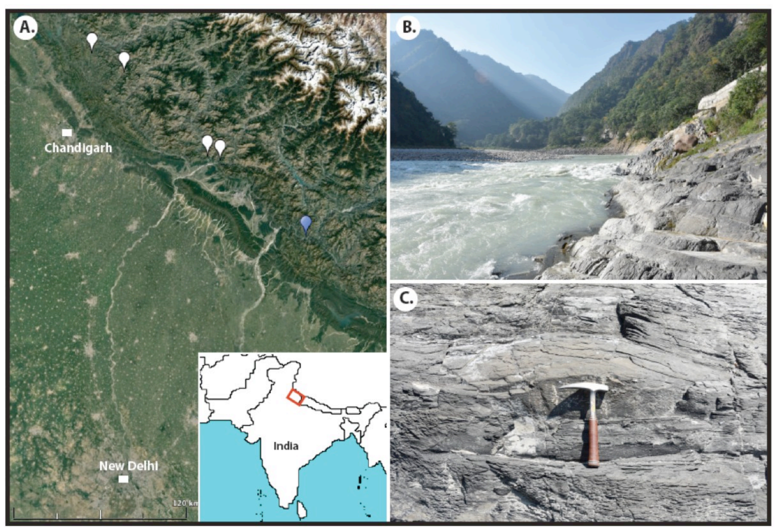

Figure 1. A) Map of study locations in Northern India (inset, red box). Shimla sites are marked in white and the Tal section in blue. B) Overview of freshly eroded Tal section along the banks of the Ganges. C) Example of Tal shale lithology.

These samples, once collected, were prepared and analyzed in the Yale Metal Geochemistry Center as part of a large compilation of Cr isotope data. Measurements were performed after column chromatographic separation procedures on a NeptunePlus multi-collector inductively-coupled plasma mass spectrometer. A detailed description of geochemical methods is available in Cole*, et al.* (9).

Results and Discussion

We observe a striking baseline shift from largely unfractionated Cr isotope values in all samples prior to ~ 800 Ma, indicative of a lack of oxidative Cr cycling, to highly fractionated values beginning in the early Neoproterozoic (Fig. 2). Specifically, samples from the Simla Group fall within the unfractionated range of bulk silicate earth (BSE), while the Tal Group shows significant fractionations beyond igneous values, ranging from 0.16 ‰ to 0.59 ‰. While the complete dataset, published in Cole et al. (2016), is temporally extensive, the focus of this project was on improving the constraints on the timing of the shift observed by Planavsky et al. (2014) from largely unfractionated Cr isotope values to highly fractionated values indicative of significant oxidative Cr cycling in the early Neoproterozoic. Thus, this study attempted to target this critical time interval preceding the diversification of animals in order to fill in this gap, making the Simla Group a critical contribution to this work. Additionally, a baseline comparison to Cr values from a time when oxidative cycling of Cr would be expected (i.e., in the Paleozoic), is necessary to make a grounded comparison to a Cr signal from a low-oxygen world. The early Cambrian Tal Group provided a major contribution in this respect, laying the groundwork for a more expanded Paleozoic Cr record. Accepting previously proposed estimates for the oxygen levels needed to induce Cr isotope fractionation, our data provide evidence for an Earth system in which baseline atmospheric oxygen levels would have been low enough to inhibit the diversification of animals until ~ 800 Ma.

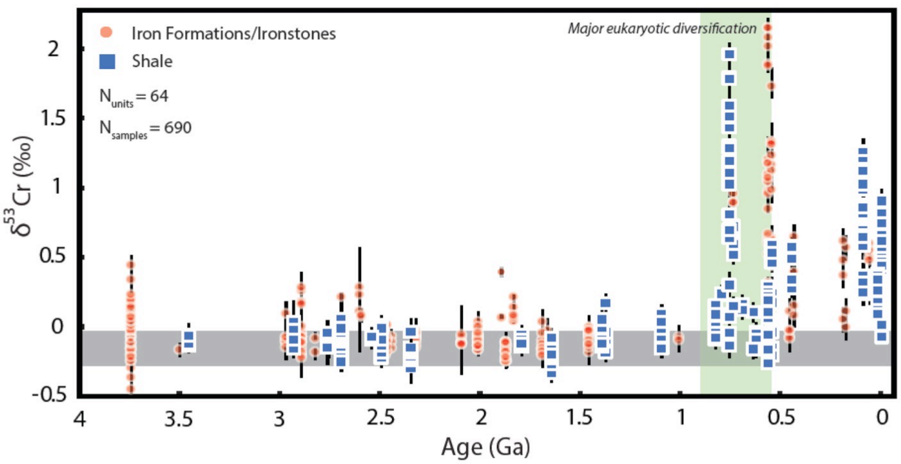

Figure 2. The shale (blue) and iron formation/ironstone (red) record of Cr isotopes through time, highlighting the transition from largely unfractionated values through the Mesoproterozoic to highly variable, fractionated values after ~ 800 Ma. The gray bar shows the range of bulk silicate earth, while the green bar highlights the period of major eukaryotic diversification based on molecular divergence time estimates and the appearance of the first body fossils. (Cole et al., 2016)

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