

Depletion of Cobalt as a micronutrient in the Eastern Equatorial Pacific

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Metal concentrations in open ocean surface waters are lower than any other environment known to support life. In the past decade, major oceanic regions were shown to be iron-limited, the importance of other trace elements is not well understood. Here we report that the geochemistry of cobalt in the Peru Upwelling region is dominated by its importance as a micronutrient. A large and previously undocumented flux of labile cobalt equivalent to 11% of the Pacific Ocean surface inventory behaved as a micronutrient with correlations with major nutrients (N, P; $r^2=0.77, 0.83$) until depleted to $\leq 50\text{pM}$ of strongly complexed cobalt. Co:P utilization ratios were an order of magnitude higher than in the North Pacific, comparable to utilization rates of zinc in other oceanic regions. Finally, cobalt speciation measurements showed that available cobalt decreased over four orders of magnitude in this region, with shifts in phytoplankton assemblages occurring at transitions between labile and non-labile cobalt. Together these findings show the importance of cobalt as a micronutrient and that cobalt scarcity and speciation may be important in influencing phytoplankton species composition and primary productivity in this environment.

Chemical and isotopic evolution of the Allende meteorite

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Individual chondrules and Ca-Al-rich inclusions (CAIs) separated from the Allende meteorite have been analyzed for the following: (1) trace element compositions of individual chondrules and CAIs, (2) their constituent minerals, and (3) Rb-Sr and Sm-Nd isotope compositions. Each chondrule and CAI were cut into two pieces; one piece was used for SEM-EDX and SIMS microprobe analyses, while the other piece was used for bulk analysis of trace element compositions and isotope analyses by ICP-MS and TIMS, respectively. Samples for bulk analysis were acid-leached with diluted HCl solutions, yielding leachates and residues that were analyzed separately. Matrices were also separated and have been analyzed by almost the same procedure as above.

REE patterns of bulk chondrules and bulk CAIs reflect the event of melting and crystallization. Sm-Nd isotope compositions of the chondrules and the CAIs are considered to give the age of crystallization.

However, mobile elements such as the alkaline elements and Pb are enriched in leachates relative to immobile elements such as REE, which are only slightly dissolved into leachates with LREE enrichment. Such a LREE enriched pattern can be explained by the dissolution of mesostasis and plagioclase with the acid leaching, but it is difficult to obtain the Rb and Pb positive spikes relative to the adjacent elements in the trace element pattern by the involvement of mesostasis and plagioclase in the acid leachate. The extent of this enrichment is distributed heterogeneously in each chondrule and each CAI. This behavior of mobile elements in the chondrules and the CAIs are attributed to secondary Fe-alkali-halogen metasomatic alteration resulting in the replacement of primary phases such as mesostasis, plagioclase, melilite and fassaite by Na-, K-, Fe- and Cl-rich phases. It is expected that Rb behaved similarly to these mobile elements during this alteration. Rb-Sr isotope systematics in chondrules and CAIs show apparent isochron ages of $4.26\pm 0.08\text{Ga}$ and $4.08\pm 0.24\text{Ga}$. These observations suggest that Rb-Sr isotope systematics and the concentrations and heterogeneity of some mobile elements have been strongly affected by the metasomatic alteration of the Allende meteorite. The timing of this event would have occurred at significantly later stage after accretion, approximately 4Ga.