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Mineralogical and geochemical changes during hydrothermal alteration of 49 Ma old basalts from the West Philippine Basin

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The 49 Ma old basaltic basement cored at Site 1201 in the West Philippine Basin during Ocean Drilling Program Leg 195 [1] suffered intense post-emplacement hydrothermal alteration. After emplacement, the volcanic basement was slowly buried by deep marine red clays, and later by a thick turbidite sequence, resulting in basement isolation from seawater. The hydrothermal alteration accounts for the growth of K-Fe-Mg-smectites (glauconite and minor Al-saponite), mixtures of Fe-oxyhydroxides and clay minerals ("iddingsite"), zeolites (natrolite group zeolites, analcite), alkali-feldspar and Ca-carbonate [2]. The secondary minerals replace primary olivine, plagioclase and glass, and fill veins and primary vesicles in the basalts. The hydrothermal alteration has also been responsible for chemical changes in the bulk rock, especially the increase of water (L.O.I. up to 6.6 wt.%; [1]) and ⁸⁷Sr/⁸⁶Sr, and uptake of alkalis. Overall, the secondary mineral paragenesis and mutual relationships suggest that the hydrothermal alteration occurred mainly within the zeolite-facies, at T ≤ 100-150°C and under oxidizing conditions, characterized by a high seawater/rock ratio, in an open-circulation regime. A later stage of alteration occurred at T ≤ 70°C, in a more restricted circulation regime, as a likely consequence of basement burial underneath the sedimentary cover, which may in turn have supplied an altered, Ca-rich and Mg-K-sulfate-poor fluid causing precipitation of secondary, almost pure, Ca-carbonate.

References

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Mo isotope fractionation in the marine environment: Theoretical considerations

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Recently, the ability to measure Mo isotope fractionation with MC-ICPMS techniques boosted new research on the Mo oceanic cycle. The Mo isotopic composition of ocean water was found to be very homogeneous, as expected from the large ocean residence time of Mo (800ka). One of the most prominent findings is, that authigenic chemical sediments contain Mo with significantly lighter isotopic composition than ocean water. (-1 permil / amu). In order to link this empirical observation to geological processes, working hypotheses on the fractionation mechanism have been established. Thereby the most recent ones propose fractionation either between different dissolved species [1] or at particle surfaces [2]. Importantly, in both hypotheses equilibrium Mo isotope fractionation is assumed. Our approach here involves theoretical ab initio calculations of expected isotope fractionation applied to Mo species mentioned in the above working hypotheses.

Equilibrium stable-isotope fractionations for the light elements can be accurately modeled in terms of the small energy difference arising from the sensitivity of the vibrational frequencies to the masses of their constituent atoms. For more complex molecules, such as (MoO₄²⁻) and the (Mo(OH)₆) complexes, the motion of the central atoms, the different vibrational modes and the sensitivity of these modes to isotopic substitution has to be taken into account. Priority will be given to a) the change from dominant MoO₄²⁻ to protonated HMoO₄⁻ (both tetrahedral, but the protonated species has a significantly elongated M-O bond) and b) change from tetrahedral HMoO₄⁻ to octahedral coordination.

If the empirical observations can be matched with calculations following process a), the Mo isotope fractionation may be explained as equilibrium fractionation between two dissolved species. A better match with model b) would require an additional process either on particle surfaces, biologically mediated or in subsurface micro-environments.

A theoretical match would support the hypothesis, that Mo isotope fractionation in sediments is definitely linked to the presence of oxygen. Thus, the present study is also important to establish combined Mo concentration and isotope fractionation data as proxy for the rise of oxygen in the early atmosphere.

References

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