On the fluid-mobility of molybdenum, tungsten, and antimony in subduction systems

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Molybdenum (Mo) and tungsten (W) have long been regarded as being more or less immobile during slab fluid-induced arc magma generation. Here we characterize about 180 samples of young, predominantly mafic to intermediate tephras and lavas for their Mo, W, and antimony (Sb) concentrations, to examine the fluid-mobility of these elements in subduction systems. Samples were taken along the active arcs of the Chilean Southern Volcanic Zone (SVZ) and the Central American Volcanic Arc (CAVA). When relating Mo, W, and Sb to trace element ratios typically used to constrain the involvement of subduction fluids in magma formation, such as Ba/La or U/Th, Mo, W, and Sb are enriched in the most fluid-influenced, highest-degree melts. W/Mo ratios correlate positively with Pb/Ce, which is established to reflect a recent subduction signal or assimilation of crustal material with an ancient subduction signature, suggesting that subduction processes promote enrichment of W over Mo. This is well expressed at the SVZ and most of the CAVA; while few OIB-type rocks from Central Costa Rica form an opposite trend. Moreover, Mo/W ratios co-vary with Cl contents derived from melt inclusions, indicating that the relative degree of mobilization responds to the composition of the subduction fluid. To evaluate the mobility of Mo, W, and Sb during metamorphism in the slab, eclogites with no or minor metasomatic overprint and a fluid-induced overprint in an eclogite-blueschist sequence were investigated. None of the three elements shows a systematic variability related to metasomatism and the minor variations are interpreted to reflect protolith heterogeneity. This suggests that Mo, W and Sb remain relatively immobile up to depths of 70 km in the subduction zone.

Long-term development of diagenetic signals of past sulfate-methane transition zones in subseafloor sediments

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Anaerobic oxidation of methane (AOM) coupled to sulfate reduction in the sulfate-methane transition zone (SMTZ) leaves prominent diagenetic carbon and sulfur signatures in pore-water and solid-phase chemistry that are preserved over geological time scales. We report on the evolution of these signals in the sediments of Site U1341 drilled during Integrated Ocean Drilling Program (IODP) to the Bering Sea to a depth of 600 meters below seafloor (mbsf). At this site, present-day microbial activity associated with organic carbon mineralization is comparably low as evidenced in low dissolved inorganic carbon (DIC) concentrations, and a minor decrease in sulfate concentrations in the top 50 mbsf. Strong decrease of sulfate concentrations below 140 mbsf mirrored by pronounced ^{34}S-sulfate enrichment at the depth of minimum sulfate concentrations suggest that the extent of microbial sulfate reduction was high in this sediment interval deposited during a period of elevated primary productivity in the water column between 2.48 and 2.56 Ma. Elevated sulfate reduction rates drove sulfate to depletion and facilitated the onset of methanogenesis, AOM and the installation of a SMTZ. Rates of these processes apparently declined as a consequence of decreased availability of organic carbon during later time periods. This interpretation is consistent with ^{34}S-enriched pyrite, ^{13}C-depleted dolomite phases and barium depletion to detrital background in distinct sediment intervals. Close examination of the diagenetic pore-water and solid-phase signals, however, revealed that their relative positions in the sedimentary sequence considerably diverge. Also, pore-water DIC, sulfate, Ca and Mg concentrations and isotope profiles do not covary systematically. Our results suggest variable responses of diagenetic signals produced by past SMTZs in the pore-water and sediment over prolonged time scales.