# Controls on isotope fractionation during sulfate reduction

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Sulfur isotopes are fractionated during dissimilatory sulfate reduction. The magnitude of fractionation is controlled by the flow of sulfur through the reaction network: $SO_4^{2-} \leftrightarrow$ adenosine-5'-phosphosulphate (APS) $\leftrightarrow SO_3^{2-} \rightarrow H_2S$, where individual enzymes operate at different efficiencies and with distinct fractionation factors. While the influence of this flow on fractionation has been modelled [1-4], the factors controlling the fractionation during the individual enzymatic steps are still poorly understood.

Using cell free extracts of *Desulfovibrio vulgaris*, we measured the fractionation during the reduction of sulfite to sulphide by the dissimilatory sulfite reductase (dsr) under different temperatures and with organic and inorganic substrates. Temperature had a greater influence on the magnitude of fractionation than substrate type. At 37°C, $H_2$ and formate produced fractionations of 18 and 15 ‰ respectively. At 25°C the magnitude of fractionation increased to 25 ‰. This was coupled to a reduction in the rate of sulfite reduction.

The fractionation during sulfite reduction by sulphate reducers who produce distinct fractionations and have different types of dsr's will be evaluated.

[1] Brunner & Bernasconi (2005) *GCA* **69**, 4759-4771. [2] Canfield *et al*. (2006) *GCA* **70**, 548-561. [3] Farquhar *et al*. (2003) *Geobiol* **1**, 27-36 [4] Hoek *et al*. (2006) *GCA* **70**, 5831-5841.

# The origin of EM1 alkaline magmas during Cenozoic reorganization of subduction zone of Kamchatka

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We report new Ar/Ar age and geochemical data on the oldest magmatic rocks from the central segment of the Eastern Volcanic Belt of Kamchatka, a neovolcanic zone formed during the Late Miocene due to migration of frontal arc volcanism in Kamchatka from the Sredinny Range to its present eastern position [1,2]. Volcanic rocks from the upper Left Zhupanova River (N54.1° E158.9°) range from older (7-12 my) LREE- and HFSE-rich alkaline and transitional basalts (La/Yb=7-38, Nb/La=0.8-1.3, Ba/Th=40-140) to younger (3-8 my) strongly calc-alkaline andesites and dacites with adakitic affinity (La/Yb=7-17, Sr/Y=53-68, Nb/La=0.40-0.65, Ba/Th=300-600). The younger calc-alkaline rocks have isotope compositions similar to the recent island-arc rocks in Kamchatka ($^{87}Sr/^{86}Sr$ = 0.7032 - 0.7034, εNd = +7.0 - +8.8, $^{206}Pb/^{204}Pb$ = 18.2-18.3, $^{207}Pb/^{204}Pb$ = 15.45 - 15.46, $^{208}Pb/^{204}Pb$ =37.7-37.9). These compositions indicate derivation from subduction-modified depleted Pacific mantle and/or through melting of the subducting Pacific oceanic plate. The older alkaline to transitional basalts range from moderately to strongly enriched OIB-like compositions with EM-1 isotope characteristics ($^{87}Sr/^{86}Sr$ = 0.7033 - 0.7044, εNd = +2.1 - +7.3, $^{206}Pb/^{204}Pb$ = 17.9 - 18.1, $^{207}Pb/^{204}Pb$ = 15.44 - 15.53, $^{208}Pb/^{204}Pb$ = 37.8 - 38.2). The EM-1 alkaline basalts are unique among the Cenozoic rocks of Kamchatka and thus are unlikely to originate from a long-lived anomalous mantle region beneath Kamchatka. The geochemically anomalous mantle region, however, could be correlated to the low-velocity mantle plume-like anomaly under Meiji Seamount mapped by seismic tomography studies [3]. Therefore, we propose that the enriched mantle flowed westward through a slab window beneath Kamchatka at the initiation of the modern subduction zone.

[1] Avdeiko *et al.* (2002) *Geotectonics* **4**, 64-80. [2] Lander & Shapiro (2007) *AGU Monograph* **172**, 57-64. [3] Gorbatov *et al.* (2001) *Geophys. J. Int.* **146**, 282-288.