

Meso-Cenozoic calc-alkaline magmatism in the South Shetland Islands, Antarctica: Implications for temporal changes of the mantle sources

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We present new Sr-Nd-Pb isotope data of the volcanic rocks from Barton and Weaver peninsulars, King George Island (KGI), Antarctica. We interpret these data in combination with previously published trace and isotope data for Meso-Cenozoic volcanic rocks in the South Shetland Islands (SSI) to gain a better understanding of the geochemical evolution of the mantle source region [1]. The studied rocks are from four volcanic islands and range in age from 143 to 44 Ma. They have high abundances of LILE and LREE relative to HFSE, consistent with products of subduction related magmatism.

The systematic inter-island variations are recognized from a comprehensive examination of the trace elements and isotopic compositions. The degree of enrichment of Sr-Nd-Pb isotopic compositions decreases towards younger samples, while the ratios of fluid-mobile elements/HFSE (Sr/Yb, Pb/Yb and U/Yb) gradually increase. We suggest that the compositional trends observed in the volcanic rocks of the SSI can be created from the addition of a relatively constant subduction component to temporally varying heterogeneous mantle sources. The higher radiogenic Pb and Sr isotopes and lower ¹⁴³Nd/¹⁴⁴Nd ratios of the older volcanic rocks from Greenwich and Livingston islands compared to younger rocks can be explained by the significant influence of enriched previously metasomatized mantle material rather than fluids or sediment melts from the subducting slab. In contrast, the geochemical nature of the youngest King George Island volcanic rocks suggests a relatively large contribution of a slab-derived fluid component to the magma generation, but a minor role of the enriched component.

[1] Machado *et al.* (2005) *Lithos* **82**, 435-453.

Oxidation state during weathering on the early Earth

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Considerable evidence has accumulated from sulfur isotopic and paleosol studies, as well as evidence from studies of detrital pyrite, siderite and uraninite, supporting a picture of an early Earth atmosphere which did not become oxygenated until about 2.4 Ga. Recent studies have suggested a rather benign atmosphere dominated by N₂ and CO₂, with minor amounts of species such as H₂, CH₄ and CO depending on the relative rates of volcanic outgassing and loss to space [1]. However, the specific f_{O₂} is not clear.

Here we emphasize that a powerful constraint on the f_{O₂} arises if we assume that the mobility of iron as Fe²⁺ inferred from paleosol studies can be extrapolated back to the earliest weathering cycle on the prebiotic Earth. Such weathering presumably involved interaction of the atmosphere with mafic or ultramafic rocks exposed as landmasses. We have carried out a series of aqueous speciation and chemical mass transfer calculations to model such interactions. Starting with a model rainwater interacting with model basaltic mineral assemblages containing iron only in silicates (as Fe²⁺) and magnetite, we established the likely ranges of f_{O₂} given different initial values of temperature (25 - 75 C), f_{CO₂}, and f_{N₂}, at all times attempting to minimize the formation of hematite (or magnetite) as a weathering product. Typical initial values of f_{O₂} found were 10⁻⁶⁸ - 10⁻⁷⁰ bars at 25 C and f_{CO₂} = 10^{-1.5} bars. Typical weathering minerals produced with moderate extents of reaction progress include diaspore replaced by kaolinite, followed by pyrite, siderite and chalcedony. The evolution of f_{O₂} from the initial value depended on the presence of magnetite as a reactant mineral in the initial basalt. Reaction with magnetite forced an increase in f_{O₂} from the initial values, which can eventually result in hematite formation. However, this reaction might be counterbalanced by simultaneous reaction with trace reducing gases, keeping f_{O₂} near 10⁻⁷⁰ bars. When f_{O₂} dips below such values (where graphite is stable but suppressed), model polyaromatic hydrocarbons (PAHs) such as pyrene may form if adequate catalysts can operate. Interestingly, during the course of the weathering the aqueous Fe concentrations can approach 10⁻⁴ m, comparable to Mg, suggesting a possible land-based source for transport of Fe to the early oceans.

[1] Catling & Claire (2005) *Earth & Planet. Sci. Lett.* **237**, 1-20.