Flux and $^{87}Sr/^{86}Sr$ of land-derived Sr to seawater – Interpreting the marine Sr isotope record

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Temporal variations in seawater $^{87}Sr/^{86}Sr$ are very well documented throughout the Phanerozoic, but are difficult to interpret. Palmer and Edmond [1], Davis *et al*. [2] and more recently Vance *et al*. [3] have used assessments of present-day river, diagenetic and hydrothermal fluxes to argue that the marine Sr system is currently not at steady state. This view is supported by combined stable and radiogenic Sr isotope analyses [4]. In contrast, Allegre *et al*. [5] argue that the missing flux of unradiogenic Sr to seawater results from weathering of volcanic arcs and ocean islands.

A critical, comprehensive review of available (more than 200 analyses) river fluxes of Sr to the oceans [6] indicates that the flux from young volcanic terrains has been underestimated [7]. However, this unradiogenic land-derived flux is likely insufficient to fully account for the missing unradiogenic Sr. The biggest unknowns regarding the land-derived Sr flux are subterranean contributions and the fact that contributions from near-coast areas have been under-sampled in most previous studies. A few examples from well-studied river systems in North America, Europe and Asia illuminate this point. As coastal areas are typically geologically younger than the continental interiors, and dissolved riverine $^{87}Sr/^{86}Sr$ correlates well with bedrock ages of drainage basins, present-day assessments of riverine Sr fluxes may be biased to more radiogenic values [6]. The present-day riverine $^{87}Sr/^{86}Sr$ is thus likely less radiogenic than the best empirical global estimate of 0.7111 [6]. Temporal variations in seawater $^{87}Sr/^{86}Sr$ likely reflect variations in the flux and $^{87}Sr/^{86}Sr$ of land-derived Sr to seawater caused by tectonic, lithologic and climatic changes of Earth's surface.

[1] Palmer & Edmond (1989), *Earth Planet. Sci. Lett.* **92**, 11-26; [2] Davis *et al*. (2002), *Earth Planet. Sci. Lett.* **211**, 173-187; [3] Vance *et al*. (2009), *Nature* **458**, 493-496; [4] Krabbenhoeft *et al*. (2010), submitted; [5] Allegre *et al*. (2010), *Earth Planet. Sci. Lett.* (in press); [6] Peucker-Ehrenbrink *et al*. (2010), *G-cubed* (in press); [7] Fiege *et al*. (2009) *Chem. Geol.* **268**, 337-343.

Zircon and titanite geochemical and age constraints on ore-related magmas

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Accessory minerals are recognized as 'small but important' geochemical tracers of petrological processes. The range of minerals to define the temperature or oxidation state of the magma/fluid is wide (e.g. rutile, magnetite, ilmenite, etc.) but zircon, titanite, and occasionally apatite and rutile are preferred due to the opportunity of reconstructing the time secession of the geochemical evolution. In present study we focus on the behaviour of zircon and titanite during processes which are important for ore-deposits: (i) magma mixing, as it can lead to magmatic volatile saturation and potentially trigger volcanic eruptions and/or the formation of magmatic-hydrothermal ore deposits, and (ii) deposit scale evolution of the magma from a single source magma chamber.

Titanite and zircons from the complex gabbro-to-granite Petrochan pluton in W Bulgaria are both dated precisely by ID-TIMS in the range 303-307 Ma. Mixing and mingling affect both accessory phases (LA-ICP-MS and EMP data): the zircons in the hybrid gabbro are typically rich in REE, U and Th; REE in titanites reflect late magmatic concurrent grow with the apatites and zircons in the hybrid varieties and a growth as an reaction phase (1.5-2 orders lower content of the LREE and one order lower HREE) in the cross-cutting lamprophyre (feeder?) dykes. Insitu εHf values of the zircons (MC-LA-ICP-MS) range from +1 to +11 with the highest values in some mafic magmatic enclaves and the gabbros.

In a Variscan granite hosting an 'intrusion related' Au (-Ag-W) mineralization (Trun region, W Bulgaria) zircons and titanites are both U-rich. The zircons show common lead rich inclusions and lead loss that hamper age determinations. After applying the 'chemical abrasion' technique and the new double spike solutions of the Earth Time project they are dated at 332.57 ± 0.60 Ma by ID-TIMS. The late magmatic titanites yield concordia age of 334.1 ± 1.2 Ma. Both minerals reveal a trace and REE-distributions that are typical for a differentiated crustal dominated magma.

In the Cretaceous magmatic belt of Bulgaria, which hosts world-class Cu-(Au)-porphyry deposits the titanite can be used complementary to the zircon as geochronometer when its radiogenic lead/common lead ratio $Pb^*/Pb_c > 0.5$.