Continental flood basalts and biotic crises: Does the Paraná-Etendeka exception prove the rule?

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The temporal correlation between continental flood volcanism and severe paleoenvironmental effects including mass extinctions are well known although the causal mechanism (s) remain unclear. Various metrics of the magnitude of either phenomenon (e.g. % taxa extinct or volume of magma erupted) define positive correlations but the extent of scatter in such relationships implies that other variables are important. Some of the larger CFB's that fail to coincide with profound extinction events (e.g. Ferrar-Karoo) turn out to be temporally distributed over several million years and their anomalously feeble impact may be due to lower effusion rates reducing atmosheric loading rates for volcanogenic volatiles. Among the largest CFB's clearly erupted mainly over a short time interval (< 3 Ma; e.g. Siberian, CAMP and Deccan), the Paraná-Etendeka province (PEP) stands out distinctly as an outlier in the correlation with biotic crises. Extensive incremental-heating Ar/Ar data demonstrate unequivocally that the PEP was brief (>90% erupted 135-132 Ma; calibration per [1]), and previous studies suggesting a protracted event spanning ~10 Ma were flawed. The resolution of this apparent conundrum may lie in the importance of thermogenic volatiles (mainly CO_2, methane and sulfates) released from country rocks during CFB events, as has been proposed in many recent studies. Virtually throughout the PEP, volcanic effusions were emplaced atop up to 450 m of eolian sands of the Botucatu and Etjo Fms., and the nearest-surface carbonaceous strata (< 80 m thick Iratí Fm.) at the time of the PEP event were >2 km beneath the surface. We suggest that thermogenic CO_2 was minimal in the PEP event due to a combination of (1) relatively sparse carbonaceous sediments in the thermal aurole; (2) depth (lithstatic pressure) of these sediments being sufficiently high to retain CO_2 in metamorphic assemblages and inhibit brittle fracturing, limiting transmissivity for thermogenic volatiles. Moreover, PEP magmas are exceptional among the largest brief CFB's in the dominance of lithospheric melt sources, suggesting minimal magmatic contributions to volatile loading of sulfates and CO_2.

[1] Renne *et al.* (2010) *GCA* **74**, 5349–5367.

Iron species in soils on a mofette site studied by Fe *K*-edge XANES

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Ascending geogenic CO_2 is a soil-forming factor on mofette sites: With increasing soil CO_2, the amounts of pedogenic Fe decrease, and Fe oxides are poorly crystalline according to extraction with oxalate and dithionite [1]. To further study the Fe speciation (especially that of Fe (II)), we applied spatially resolved X-ray absorption near-edge spectroscopy (XANES) to soil samples from a mofette site in the NW Czech Republic. The samples originated from spots with 4 and 100% CO_2 in the soil atmosphere. Point XANES spectra (1 μm^2) at the Fe *K*-edge (7112 eV) were collected at beamline ID 21 of the ESRF, Grenoble, in fluorescence mode. Altogether, we recorded 73 spectra on regions of interest identified from 5 fluorescence maps of 3 thin sections prepared from undisturbed soil samples. Linear combination fitting of reference spectra from a whole of 51 references including various Fe (II)- and Fe (III)-bearing minerals and organic species was used for Fe-species identification. In almost all cases, two references were sufficient as checked by the sum of squared differences.

The Fe-fluorescence maps explicitely showed a heterogeneous spatial distribution of Fe with accumulation in larger pores (e.g. former root channels) and depletion in the soil matrix. We conclude small particles (< 1 μm), because point spectra could not be explained by a single reference spectrum. We identified smectites, illite and ferrihydrite in the Fe-accumulation zones. Iron in the Fe-depletion zones was mostly present in clay minerals such as different smectites, illites and chlorites in 68 spectra. Especially at 100% CO_2, we identified Fe (II)-containing minerals such as green rust, vivianite, siderite and magnetite in the soil matrix. According to XANES, Fe sulphates and Fe sulphides were not present. We detected only slightly more Fe (II) complexed by organic species at 4% CO_2 than at 100% CO_2 indicating that CO_2 impedes the association of organic matter with Fe-containing minerals. This is in line with the observation of mainly non-decomposed, probably particulate organic matter in soils on mofette sites and only a small fraction of organo–mineral associations [1].

[1] Rennert *et al.* (2011) *Eur. J. Soil Sci.* in press