Derivation of a new soil respired CO_2 proxy for application to paleo-CO_2 reconstruction

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One way to predict future climate change is by studying warming events in the geologic past. The main control of the Earth's temperature over geologic time is the concentration of atmospheric CO_2; however, the precise amount of CO_2 in the past is not fully understood [1]. Therefore, it is essential to quantify the atmospheric CO_2 concentration in the geologic past, especially at times of rapid climate change analogous to current changes.

The widely applied paleobarometer introduced by Cerling [2] calculates atmospheric CO_2 based on the isotopic ratio of pedogenic carbonates precipitating in equilibrium with soil CO_2. Its primary source of uncertainty is the amount of soil respired CO_2 in the paleosol at the time of pedogenic carbonate formation. To remove the uncertainty from the Cerling [2] paleobarometer, a new soil respired CO_2 proxy was calibrated for soils and paleosols. The relationship between modern soil CO_2 and mean annual precipitation was derived from an extensive literature review of modern carbonate bearing soil CO_2 data. Based on 580 measurements of summer soil CO_2 (time of carbonate formation) from 21 pedogenic carbonate-bearing soils, we find a linear relationship between summer levels of soil respired CO_2 and MAP ($r^2 = 0.63$; SE = 1126 ppm). For paleosols, past soil respired CO_2 can be predicted using MAP estimates calculated from either the depth to Bk horizon [3] or the chemical index of alteration without potassium [4].

During the Middle Miocene Climatic Optimum (16Ma) we see elevated atmospheric CO_2 levels analogous to the future rise in CO_2 over the next century [5]. Here we use this new soil respired CO_2 proxy to reconstruct atmospheric CO_2 during the middle Miocene from Montana and compare these results to previously published estimates from Montana and Kenya during this time period [5], [6].

[1] IPCC (2007) *Synthesis Report,* 104 pp. [2] Cerling (1991) *American Journal of Science* **291**, 377–400. [3] Retallack (2005) *Geology* **33**, 333–336. [4] Sheldon, Retallack & Takana (2002) *Journal of Geology* **110**, 687–696. [5] Retallack (2009) *Palaeogeography, Palaeoclimatology, Palaeoecology* **281**, 57–65. [6] Ekart, Cerling, Montanez & Tabor (1999) *American Journal of Science* **299**, 805–827.

Basaltic glasses as records of mantle oxygen fugacity

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Several petrological lines of evidence indicate that basalts from different tectonic environments (MORB, BABB, OIB, arcs) express different inherent oxygen fugacities. It is ambiguous whether fO_2-diversity derives from the mantle source or shallow processing. $Fe^{+3}/\sum Fe$ ratios of primitive, undegassed basaltic glasses and naturally glassy olivine-hosted melt inclusions, determined using μ-XANES [1], may reflect the oxygen fugacity of the mantle source. Major, trace, and volatile elements, and isotopic ratios measured on the same glasses, allows us to interrogate the influences on mantle and magmatic redox.

$Fe^{+3}/\sum Fe$ ratios of MORB glasses are 0.16 ± 0.01 (n=60), higher than reported by micro-colorimetry (0.07±0.03) [2] or direct titration (0.12±0.02) [3]. Only 0.01 (absolute) of the XANES/wet-chemistry disparity can be attributed to our Mossbauer-based XANES calibration, and may derive from differences in the material being sampled and the influence of FeO* uncertainty on wet-chemical determinations. MORB glasses record olivine control of $Fe^{+3}/\sum Fe$ ratios. Primitive glasses, with only olivine on the liquidus, are traced back to primary mantle melts by incrementally adding equilibrium olivine until equilibrium with Fo_{90} is reached, and then referenced to fO_2 [4]. Primary MORB magmas indicate fO_2 of QFM -0.25 ± 0.18 (referenced at 1200°C, 1 atm).

Calculated primary melts for the most primitive arc melt inclusions from the Marianas reflect QFM +0.84 ± 0.22 while BABB varies between arc and MORB sources as a function of primary melt water content – mirroring the correlation seen in the raw $Fe^{+3}/\sum Fe$ ratios [5]. We show that degassing and crystallization cannot be responsible for these observations. The influence of the oxidized plate appears to persist through plate recycling. Samoan lavas are more oxidized than average MORB, and their $Fe^{+3}/\sum Fe$ ratios correlate with EM2-type isotopic enrichment that can be attributed to hydrated, oxidized, subducted sediment.

[1] Cottrell *et al.* (2009) *Chem. Geol.* **268**, 167–169. [2] Christie *et al.* (1986) *EPSL* **79**, 397–411. [3] Bezos & Humler (2005) *EPSL* **69**, 711–725. [4] Kress & Carmichael (1991) *CMP* **108**, 82–92. [5] Kelley & Cottrell (2009) *Science* **325**, 605–607.