The source of carbon in cave air CO_2 under mixed woodland and grassland vegetation

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We measured concentrations and stable carbon isotope compositions of CO_2 in the atmospheres of several caves in central Texas and southern Arizona in order to identify the sources of CO_2 -carbon. The vegetation above all of the caves studied is a mixture of grasslands (C_3 and C_4 vegetation) and woodlands (dominantly C_3 juniper and oak trees). We tested the hypothesis that the deepest rooting plants have a dominant influence of the $\delta^{13}C$ value of CO_2 in the caves. Within caves, we monitored CO_2 at individual locations on monthly and daily time-scales. We also measured CO_2 in the pore spaces of soils dominated by different vegetation types above each cave. The $\delta^{13}C$ value of respired CO_2 ($\delta^{13}C_r$) was calculated for all gas samples from the measured $\delta^{13}C$ values and CO_2 concentrations by rearranging equations derived by Davidson[1]. The sources of cave CO_2 were then identified by comparing soil and cave air $\delta^{13}C_r$ values. In three of the caves, mean cave air CO_2 $\delta^{13}C_r$ values were within 0.5 ‰ of mean $\delta^{13}C_r$ values in woodland soils (-23 to -24‰ vs VPDB), even when measured $\delta^{13}C$ values of cave and soil CO_2 were different by up to 2.5‰. The $\delta^{13}C_r$ values in grassland soils above these three caves were 3-5 ‰ higher than cave and woodland soil values. In one cave covered primarily by grassland and roads, the cave $\delta^{13}C_r$ values were intermediate between grassland and woodland values. When cave-air CO_2 concentrations were below 1000 ppmV, cave $\delta^{13}C_r$ values were more negative than woodland soil values by 20‰ or more, likely the result of preferential degassing of $^{12}CO_2$ from CO_2-supersatured drip water[2]. The consistent agreement between soil and cave air $\delta^{13}C_r$ values indicate that the same mixing and diffusion equations, which are used to calculate $\delta^{13}C_r$ and have been previously applied to soils, also apply to cave atmospheres. Our results suggest that unless cave CO_2 concentrations are <1000 ppm the majority of CO_2 advects or diffuses into these caves from soils as a gas rather than being transported in aqueous solution. Calculated $\delta^{13}C_r$ values suggest that juniper and/or oak trees supply most of the carbon to CO_2 in the atmospheres of these caves, likely because these trees have deeper roots than the other plants in these ecosystems. A one-dimensional numerical model of CO_2 production and diffusion that uses depth-dependent $\delta^{13}C_r$ values as input supports our empirical results and our hypothesis that deeply rooted trees control the $\delta^{13}C_r$ values of cave air CO_2, even if deep respiration rates are small compared with those in the shallow subsurface. We further suggest that if a vegetation signal is archived in the carbon isotope composition of speleothem calcite, then it may be biased toward deep-rooted plants.

[1] Davidson (1995) *Geochimica et Cosmochimica Acta* **59**, 2485-2489. [2] Spötl et al. (2005) *Geochimica et Cosmochimica Acta* **59**, 2451-2468.

Sulfide-silicate partitioning of PGEs (and Au): Implications for noble metal behaviour in magmatic systems

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There is considerable variation in sulfide-silicate melt partition coefficients for the noble metals (PGEs and Au), with most direct measurements (analysed by bulk methods) yielding values of 10^4 or less [e.g., 1]. More recent estimates, which combine separate metal solubility measurements in sulfide and silicate, have suggested partition coefficients exceeding 10^7 [2,3]. Resolving this discrepancy is essential for developing accurate models of noble metal behaviour during melting, and validating metal concentration mechanisms in magmatic systems.

In this study, sulfide and silicate were equilibrated at known fO2-fS2 conditions, with run-products analysed by LA-ICPMS to ensure exclusion of sulfide contamination from the silicate melt analysis. Experiments were done at 1200 deg. C and 1 atm with fS2 controlled using the Pt-PtS buffer and fO2 estimated to be FMQ-1. Three different synthetic basalts were employed, differing in their FeO content (5-15 wt%), with the added sulfide melt composition having FeS stoichiometry + 1 wt% each of Cu and Ni. Glass + sulfide were packed in crucibles made from natural chromite, then loaded, along with the sulfide buffer, in silica ampoules, which were evacuated, then sealed. Samples were held for 1 to 4 days at temperature, then quenched in cold water. Run-product glasses were free of obvious sulfide contamination, as evidenced by uniform, and low time-resolved signals for the PGE and Au.

Concentrations of Ru and Os in run-product glasses were always below detection (approx 20 and 5 ppb, respectively), yielding minimum sulfide/silicate partition coefficients of >10^5 (Ru) and >10^6 (Os). Measurable, but low, abundances for other PGE and Au were determined, with calculated sulfide/silicate partition coefficients of >10^5 (Pd, Rh, Ir, Pt) and 4000-11000 (Au). Partition coefficients for Pd, Rh, Ir and Pt were found to increase with increasing concentrations of these elements added to the sulfide melt, with little or no change in the silicate melt concentration. This is interpreted to reflect a low level of sulfide contamination in the silicate melt, and argues for even higher partition coefficients for these elements. Thus, results are in line with the large partition coefficients estimated from combined sulfide and silicate PGE solubility data. Application of these data to sulfide-saturated partial melting models yields levels of PGE and Au in calculated melts which are much lower than observed for MORB or OIB; only at the point of near complete sulfide exhaustion are calculated and observed abundances similar. An alternative to residual sulfide, such as a combination of olivine, chromite along with an alloy phase, may be required to account for levels of these elements in oceanic basalts.

[1] Fleet *et al* (1999) Lithos **47**, 127–142. [2] Andrews & Brenan (2002) *Chem Geol* **192**, 163-181. [3] Fonseca et al (2009) *GCA* **73**, 5764–5777.