Decoupling of the sub-basinal CO_2 and He mantle fluxes as evidenced by intense $CO_2/^3He$ fractionation of natural gases from Brazilian south Atlantic margin basins

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Fluxes of mantle CO_2 in sedimentary basins are of present concern regarding deep basin oil and gas exploration. Such degassing of the mantle, although of lower amplitude than that of MOR and convergent margin magmatism, has some influence on the global carbon cycling and on the carbon mass balance of sedimentary basins.

Nearly 150 samples of various basins of the Brazilian Atlantic margin have been analyzed for their molecular composition, stable isotopic ratios of carbon, hydrogen and of the nobles gases ($^3He/^4He$, $^{40}Ar/^{36}Ar$). The gases analyzed show a full compositional range corresponding to the mixing of thermogenic gas (average $\delta^{13}C_{CH4\text{-}PDB}$ = -39‰) with inorganic CO_2 (average $\delta^{13}C_{CO2\text{-}PDB}$ = -5.5‰), with CO_2 contents from 0.1 up to 78%. The $^3He/^4He$ ratio shows a consistent increase with the CO_2 concentration from $3.4e^{-7}$ up to $8.9e^{-6}$. The $CO_2/^3He$ ratio of the richest CO_2 samples is reaching that of MORB between $1.2\text{-}1.6e^9$. A decreasing trend in the $CO_2/^3He$ ratio defined by the whole sample set correlates with decreasing $^3He/^4He$ ratio and CO_2 abundance. The data support a large scale loss of CO_2 (of up to 99%) from an initial mantle fluid during its ascent towards the surface, in addition to mixing of this fractionated fluid with thermogenic gases from within the basins.

The potential loci and processes of this fractionation are discussed along with their consequence for the relative fluxes of mantle C and He to sedimentary basins.

Interactions of Arsenic and Chromium with Struvite During Mineralization

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Struvite ($MgNH_4PO_4{\cdot}6H_2O$, MAP) recovered from wastes may be a viable alternative to phosphate fertilizers [1]. However, the potential for sorption of trace elements in wastes with struvite has not been fully addressed. This study evaluates the sorption of arsenic (As) and chromium (Cr) with struvite as impacted by oxidation state, pH and initial solution concentration [2, 3]. The As content of struvite precipitated in the presence of As(V) as AsO_4^{3-} and As(III) as AsO_3^{3-} increased with pH from 8-11. Struvite recovered from As(V) solutions had As concentrations greater than fertilizer limits over the entire pH range. X-ray absorption fine structure (XAFS) analysis revealed that As(V) was coprecipitated into the struvite structure, and that As(III) was adsorbed to the mineral surface. Oxidation state also dictated Cr sorption with struvite precipitated in the presence of Cr(III) as Cr^{3+} and Cr(VI) as CrO_4^{2-} at concentrations of 1-100 μM. Less Cr was associated with struvite recovered from Cr(VI) solutions compared to Cr(III) solutions over the range of concentrations. For struvite formed in the presence of Cr(III), XAFS confirmed the formation of adsorbates at low initial Cr concentrations, with surface precipitates dominating at higher solution concentrations. Where surface precipitates were detected, the Cr content of struvite exceeded the limit for fertilizers. Fourier transform infrared analysis (FT-IR) suggested that Cr(VI) may be adsorbed and/or coprecipitated with struvite. The extent and mechanisms of sorption for As and Cr have implications for the use of struvite as a fertilizer. Coprecipitated As(V) and precipitated Cr(III) are likely to be delivered to agricultural soils along with struvite, introducing contamination to soils and plants. Conversely, low concentrations of As(III) and Cr(VI) pose less of a risk, and adsorbates may be removed from the struvite surface prior to application.

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