Densities of dilute coenzyme M solutions to 0.80 MPa and 353.15 K

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Sodium 2-mercaptoethanesulfonate ($C_2H_5NaO_3S_2$), also known as coenzyme M is a thiol that is essential to the process of methanogenesis [1]. Coenzyme M is a cofactor involved in methyl transfer reactions within methanogenic archaea. Given that fossil evidence of methanogenic archaea may date back to 2.8 billion years [2], methanogenesis is likely an ancient metabolic process. Determining the thermodynamic properties of coenzyme M is essential for understanding the potential for its formation and reaction properties in high P-T environments that host extremophiles and may have hosted the emergence of life.

The volumetric properties of dilute aqueous solutions of coenzyme M (0.09966 m, 0.19950 m, 0.299921 m & 0.39815 m) were obtained using an Anton Paar DMA 5000 vibrating tube densimeter. Reproducibility of density measurements was $<\pm 0.00002$ g·cm^{-3}, exceeding propagated errors associated with uncertainty in the measurement of temperature, pressure, and fluid concentration.

Experimentally determined volumetric properties of coenzyme M have not been previously reported in the literature. Figure 1 shows partial molar volumes at infinite dilution (V^∞) derived from fluid density data; it is clear that V^∞ is not a sensitive function of pressure in the range examined.

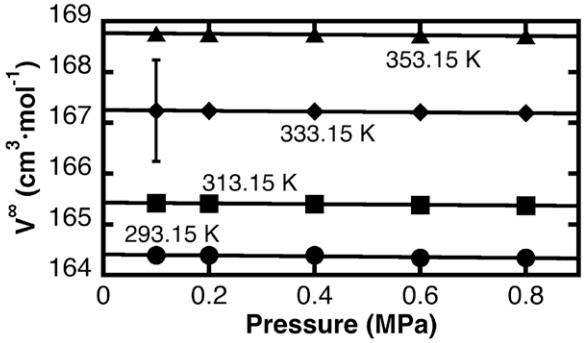

Figure 1. Experimentally determined partial molar volumes at infinite dilution of sodium 2-mercaptoethanesulfonate in aqueous solutions at 0.10-0.80 MPa and 293.15-353.15 K from this study. Lines represent simple linear regression fits to the data. The error bar represents the estimated uncertainty of ±1.0 cm^3·mol^{-1}.

[1] Balch & Wolfe (1979) *J. Bacteriol.* **137**, 256-263. [2] Brocks *et al* (1999) *Science* **285,** 1033-1036.

Deep carbonate recycling and metasomatic enrichment of the sub-continental lithospheric mantle inferred from mantle xenoliths of the East African Rift system

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The source region of the extensive magmatism driving the East Africa Rift System (EARS) is thought to involve one or more deep-seated mantle plumes with variable interactions with overlying crust and, in particular, sub-continental lithospheric mantle (SCLM). To assess the role of SCLM in modulating the volatile systematics of plume-related material, we report new results on the He-CO_2-N_2 isotope and relative abundance of mantle xenoliths from throughout the EARS (Red Sea, Ethiopia, Kenya and Tanzania).

Our analytical approach involves crushing mafic crystals to release CO_2 and N_2 trapped in fluid inclusions. This approach was used on a suite of gas-rich xenoliths (dominantly pyroxenites, n=25). The xenoliths display a large range in He-isotopes (5.9 to 13.9R_A) but have a limited range of $\delta^{13}C$ values (-3.3 to +0.8‰), with only two xenoliths showing values lower than -2‰. $\delta^{15}N$ values range from -4.11 to +5.89‰ and $CO_2/^3He$ and CO_2/N_2 ratios vary by orders of magnitude from 0.020 to 7.0 (x10^9) and 0.42 to ~3800, respectively.

The $\delta^{13}C$-$CO_2/^3He$ systematics of the xenoliths fall on a 2-component mixing line where the low $CO_2/^3He$ endmember is ~3x10^8, significantly lower than the DMM value (~2x10^9) This low ratio is consistent with low-end estimates of DMM and the mean $CO_2/^3He$ ratio of E-chondrite [1]. Thus, our new data are consistent with enrichment of the SCLM by CO_2-rich mantle fluids with $CO_2/^3He$ ratios >>3x10^8 and $\delta^{13}C$ ~0‰ - characteristics of recycled C from subducted carbonatitic material. Such CO_2 enrichments are also associated with positive $\delta^{15}N$ values reinforcing the link between the metasomatic fluid and subduction. Notably, xenoliths with high $^3He/^4He$ ratios (Afar) are also associated with $\delta^{15}N$ > -5‰, implying an important role for the deep-seated Afar mantle plume in supplying recycled volatiles to the SCLM. Oxygen isotope analysis (in prep) will further enable us to constrain the nature of the recycled component.

[1] Marty & Zimmerman (1999) *GCA* **63**, 3619-3633.

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