Stable isotopes and radiocarbon as tracers of atmospheric methane sources

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Recent studies have suggested that CH_4 emissions in urban areas may be underestimated, probably because most regional models to estimate CH_4 fluxes are based largely on agricultural emissions factors [1]. Other studies have proposed that increased extraction and use of natural gas, specifically from shale formations, may increase total methane emissions from fossil fuel sources [2,3]. In this presentation, we will demonstrate the use of stable isotopes (^{13}C and D) and radiocarbon (^{14}C) as tracers of sources of CH_4 in Los Angeles, California [4]. As expected, measurements of the $\delta^{13}C$ and δD of CH_4 from discrete sources showed separation between fossil fuel-derived sources, such as vehicle emissions, power plants, oil refineries, landfills, and sewage treatment plants and biological sources like cows, biofuels, landfills, sewage treatment plants, and cattle feedlots. We also implemented high-altitude monitoring of well-mixed air using continuous tunable laser spectroscopy measurements of CH_4 concentration combined with isotope analyses (^{14}C, ^{13}C, and D) of discrete samples. Our data, particularly variation of δD and (to a lesser extent) $\delta^{13}C$ with CH_4 concentration, indicate that the major source of excess CH_4 in Los Angeles is leakage of fossil fuels, such as from geologic deposits, natural gas pipelines, oil refining, and/or power plants. This is in contrast to some previous studies that have shown that landfills and waste treatment are the dominant source of CH_4 in urban areas. California state inventories currently lack urban emissions factors. More research is needed to constrain fluxes of this "fugitive" CH_4 from gas distribution and refining, as this flux may increase with greater reliance on natural gas and biogas for energy needs. The combination of high-resolution tunable laser concentration measurements and precise stable isotope measurements made via mass spectrometry is a very promising and powerful tool for verifying reductions in greenhouse gas emissions and constraining regional-scale emissions inversion models.

This presentation will include an overview of methods for using isotopes for source apportionment for atmospheric methane, a discussion of previous studies that have successfully applied these methods, and potential applicability to studies of shale gas extraction.

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Major element incorporation into apatite: implications for thermometery

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Apatite is a ubiquitous accessory mineral that crystallizes in a wide variety of melts from basaltic to granitic. Apatite may also grow in low temperature (~40°C) aqueous solutions and during metamorphism. Crystals incorporate a variety of trace (e.g., rare earth elements [REEs], Sr, U, Th), minor (e.g., Mn) and major (e.g., Fe, Mg, Si) elements that may be used to trace the evolution of rocks, including magma volatile contents [1-4]. It is widely accepted that the incorporation of elements into minerals is at least sensitive to temperature [3]. Therefore, understanding and interpreting the chemisty of apatite crystals (e.g, REEs, U, Th, F, C, OH, Cl, S) may be extended by knowledge of the crystalization temperature.

We report synthesis experiments of apatite crystals grown in melts from 800 to 1200 °C and pressures of 1 and 2 GPa. Synthetic and natural silicate mixes (including SUNY MORB e.g., [5]) were doped with excess moles of CaO, P_2O_5, F, ±Cl, ±S to ensure apatite saturation. Major and minor element concentrations in apatites and co-existing phases (including quartz, diopside, augite, tremolite, and glass) were characterized by electron microprobe. Preliminary data suggest that some major rock forming elements (e.g. Si, Fe, Mg) correlate with temperature when a phase is present that buffers the activities of system components containing these elements. In experiments that contain only apatite and glass, major element concentrations are still demonstrably sensitive to temperature, though component activities are not well constrained.

Elements which are structurally accommodated by the apatite lattice, coupled with component activities that are 'buffered' by other assemblages – in nature and in laboratory experiments – are likely to be the most promising candidates for apatite thermometry. As an example, the activity of SiO_2 in most (silicate) melts can usually be constrained. However, application of apatite Si contents as a thermometer may be hindered because the entry of Si into the P site requires charge compensation with other elements (e.g., trivalent REEs satisfy this requirement). Other elements such as Mg and possibly Fe, for example, may be better candidates that require fewer assumptions. Nevertheless, an apatite thermometer will require an estimate of component activities for application.

[1] McCubbin *et al.* (2010) *PNAS* **107**, 11223-11228. [2] Boyce *et al.* (2010) *Nature* **466**, 466-469. [3] Watson and Green (1981) *Earth Planet. Sci. Lett.* **56**, 405-421. [4] Spear and Pyle (2002) *Rev. in Min.* **48**, 293-335. [5] Richter et al. (2003) *GCA* **67**, 3905-3923.