Quantifying the relative contribution of natural gas fugitive emissions to total methane emissions in Colorado, Utah, and Texas using mobile $\delta^{13}CH_4$ analysis

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Fugitive emissions of methane into the atmosphere are a major concern facing the natural gas production industry. Because methane is more energy-rich than coal per kg of CO_2 emitted into the atmosphere, it represents an attractive alternative to coal for electricity generation, provided that the fugitive emissions of methane are kept under control. A key step in assessing these emissions is partitioning the observed methane emissions between natural gas fugitive emissions and other sources of methane, such as from landfills or agricultural activities. One effective method for assessing the contribution of these different sources is stable isotope analysis, using the $\delta^{13}CH_4$ signature to distinguish between natural gas and landfills or ruminants. We present measurements of mobile field $\delta^{13}CH_4$ using a spectroscopic stable isotope analyzer based on cavity ringdown spectroscopy, in three intense natural gas producing regions of the United States: the Denver-Julesburg basin in Colorado, the Uintah basin in Utah, and the Barnett Shale in Texas. Mobile isotope measurements of individual sources and in the nocturnal boundary layer have been combined to establish the fraction of the observed methane emissions that can be attributed to natural gas activities. The fraction of total methane emissions in the Denver-Julesburg basin attributed to natural gas emissions is 78 +/- 13%. In the Uinta basin, which has no other significant sources of methane, the fraction is 96% +/- 15%. In addition, preliminary results in the Barnett shale, which includes a major urban center (Dallas), are presented.

Experimental characterization of replacement symplectites: The influence of temperature and small amounts of water on microstructure evolution

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Symplectite microstructures are a widespread phenomenon in a multitude of different parageneses in metamorphic rocks. The aim of this study is to characterize the formation of symplectites and to investigate experimentally the influence of temperature and water content on the evolution of symplectite microstructures.

Synthetic monticellite (Mtc) crystals with an excess forsterite (Fo) component of about 8 mole% were annealed in a piston-cylinder apparatus at 1.2 GPa, 950 - 1200°C, run durations of 5min - 24h and water contents of 0 - 1.0 wt.% H_2O using Al_2O_3 as a pressure medium. At these conditions Mtc breaks down into two types of fine-grained symplectite microstructures.

The two symplectite microstructures can be explained by two types of cellular segregation reactions: (a) The Mtc precursor phase (Mtc I) is replaced by a symplectite (type I) consisting of Fo rods in a Mtc matrix without excess Fo component (Mtc II). (b) A symplectite (type II) consisting of a lamellar intergrowth of merwinite (Mw) and Fo is formed. In both cases replacement of the Mtc precursor phase by the symplectite implies chemical diffusion within the advancing reaction front.

The lamellar spacing of both symplectites shows a strong temperature dependence. At identical run durations the spacing of Sy I increases from 450 nm at 1000°C to 1200 nm at 1100°C, whereas the Sy II spacing increases from 250 to 400 nm. Both symplectite microstructures could only be produced in experiments with at least minute amounts of water. Adding H_2O to the experiment strongly increases the reaction rate of the symplectite formation.

Applying the formalism introduced by Degi *et al.* [1] yields a diffusion coefficient for MgO and CaO within the reaction front of around $7*10^{-13}$ m^2/s for the formation of the Sy II indicating very fast diffusion inside the reaction front.

[1] Degi *et al.* (2009), *Cont. Min. Pet.*, **159**, 293–314

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