3.3.12

Genesis and migration of nitrogen-rich gases in the North German Basin

B. MINGRAM[1], V. LÜDERS[1] AND P. HOTH[2]

[1] GeoForschungsZentrum, Potsdam, Germany; (birgit@gfz-potsdam.de; volue@gfz-potsdam.de)
[2] BGR, Berlin, Germany (P.Hoth@bgr.de)

The North German Basin (NGB) forms part of the Mid European Basin where natural gas sourced mainly from coal-bearing strata and marine shales of Carboniferous age. In the eastern part of the NGB, the nitrogen content in natural gases can reach up to 90 %. The origin of the large nitrogen contents of these gases are controversy discussed. Possible sources are sedimentary organic matter, fixed ammonium, magmatic or metamorphic rocks or primordial nitrogen.

Our study mainly focuses on C_{org}-rich Carboniferous, especially Namurian shales in order to characterize the primary total and fixed nitrogen potential and possible release processes. The study is based on a combination of mainly geochemical methods such as clay mineralogy, vitrinite reflectance, and determination of organic and inorganic fixed nitrogen, stable isotopes of nitrogen and carbon, and fluid inclusion analyses. Samples from different Namurian basins allow the comparison of shales deposited under different facies conditions, and different degree of thermal maturity. Fluid inclusions in quartz, fluorite, and calcite veins have been analyzed in order to obtain information about their fluid and gas compositions.

Indications were found for potential nitrogen storage during diagenesis and release during burial metamorphism and/or hydrothermal processes. Results indicate a deep burial of fixed ammonium up to low grade metamorphic conditions. The total nitrogen content of the organic rich Carboniferous shales reach 3000 ppm with an inorganic fixed nitrogen portion (in the form of NH_4-N) of more than 60 %. The nitrogen stable isotopic composition ranges from +1‰ up to +3.5‰. Marine Namurian shales are especially enriched in nitrogen.

Some Namurian shales show a significant decrease of fixed ammonium down to 500 ppm coupled with a shift in $\delta^{15}N$ from +3‰ up to +6‰ which suggest a release of nitrogen on a large scale. Calculation of nitrogen loss and isotopic fractionation indicate that up to 40 % of nitrogen was released as ammonia during metamorphic/hydrothermal overprint. Released NH_3-NH_4 may be oxidised during upwards migration through the red beds of the Rotliegend section. P-T information from fluid inclusions combined with subsidence data give evidence of different phases of hydrocarbon migration. Reconstructed low pressure trapping conditions of the common N_2-rich inclusions within the Rotliegend sections indicate nitrogen migration due to tectonic uplift during phases of basin inversion.

3.3.13

Methane production during metamorphism of graphitic pelites, Black Hills, U.S.A.

P.I. NABELEK[1], M. WILKE[2] AND T.A. HUFF[1]

[1] Dept. Geological Sciences, University of Missouri, Columbia, MO 65211, USA (nabelekp@missouri.edu)
[2] Institut für Geowissenschaften, Universität Potsdam, 14415 Potsdam, Germany

Carbonaceous pelites are often caught-up in convergent orogens where they can undergo high-temperature metamorphism. It is known that as cabonaceous material thermally matures and eventually turns to graphite, carbonic fluid species are generated. However, it is still unknown if significant carbonic fluid generation continues after graphitization of organic matter. We examined the isotopic composition of disseminated and vein graphite and compositions of fluid inclusion in quartz veins in metasedimentary rocks in the Black Hills, USA. The resulting data provide evidence for fluids that were generated during regional metamorphism associated with the convergent Trans-Hudson orogeny and intrusion of late-orogenic Harney Peak Granite (HPG). Regional metamorphism reached at least garnet-biotite conditions, whereas in the aureole of HPG, second-sillimanite-grade conditions were reached. $\delta^{13}C$ values of disseminated graphite range from –27.5 to –20.8‰. Graphite on the heavy side of the range is in metapelites from which significant graphite was lost and garnet growth occurred during regional metamorphism. The shift toward heavier carbon can be attributed to production of CH_4 during fluid-present metamorphism because it is isotopically lighter than coexisting graphite. Methane production occurred under fO_2 conditions that were significantly below the FMQ buffer, as evidenced by coexising magnetite-ilmenite compositions. Under these conditions, CH_4 is predicted to be the the dominant fluid species. However, the fluid composition appears to have been buffered to higher H_2O/CH_4 ratios and fO_2 by progress of metamorphic reactions. The CH_4-rich fluid was trapped as inclusions within quartz veins. CO_2-rich inclusions reflect more elevated fO_2 conditions that probably existed later during metamorphism. Vein graphite occurs in the aureole of HPG. Its $\delta^{13}C$ is ca. –17‰ and of selvage graphite, that commonly coexists with metasomatic tourmaline within host metapelites, ca. –22‰. These compositions suggest progressive precipitation of graphite from a CH_4-rich magmatic fluid that became reduced as it moved from the magma into the country rocks.

This study shows that CH_4 is likely to be an abundant species in pelitic terranes undergoing metamorphism. The high proportion of CH_4 in the fluid in the Black Hills may be the results of early decomposition of organic matter during incipient metamorphism and subsequent buffering by metamorphic reactions.