Carbon and nitrogen isotope measurements of gas-bearing fluid inclusions

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For simultaneous measurement of natural gases (N_2, CH_4, and CO_2) in fluid inclusions a sample crusher and an Elemental analyser (EA) combustion-IRMS system was used, including an EA, ConFlo III and Delta^{plus}XL mass spectrometer (Fig. 1). The general design of the crusher and its connection to an EA was adopted from Vonhof et al. (2006) and developed by GFZ machinists. The crusher is coupled to the EA via a He carrier gas line from which the carrier gas, He 5.0, passes through the crusher with 300 ml/min. The crusher consists of a special hardened steel chamber and piston which is not only useful for soft minerals, such as calcite, fluorite and ates but also for quartz and other silicates. Similar to the Amsterdam device, the GFZ crusher is equipped with a septum port for direct injection of gases for blank runs. The crusher volume of about 2 cm^3 allows crushing of up to 1g of sample material.

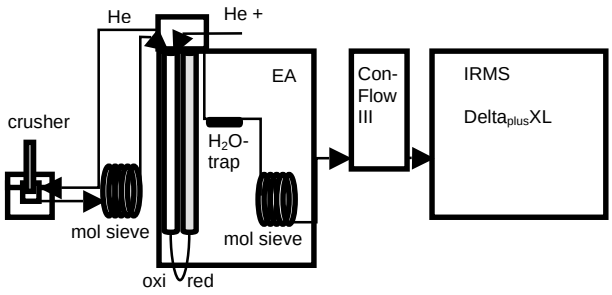

Fig. 1. Schematic diagram of the crusher-EA-IRMS line for simultaneous measurement of N_2, CH_4, and CO_2 gases released from fluid inclusions by crushing.

After crushing of sample chips (which have been used for microthermometry and laser-Raman spectroscopy before), the He – gas mixture passes through a mol sieve and separates N_2, CH_4 and CO_2 from each other. The gas species enter the oxidation column of the EA, where CH_4 gets oxidized to CO_2 with simultaneous injection of O_2 at 960°C. In order to obtain complete oxidation of CH_4, a 25 ml oxygen loop was used for the He-O_2 purge line. After passing the reduction column and water trap, the gas species N_2, CO_2 from CH_4 oxidation and original CO_2 from inclusions are separated again in a second mole sieve and enter the isotopic ratio mass spectrometer (IRMS) via a Conflo III.

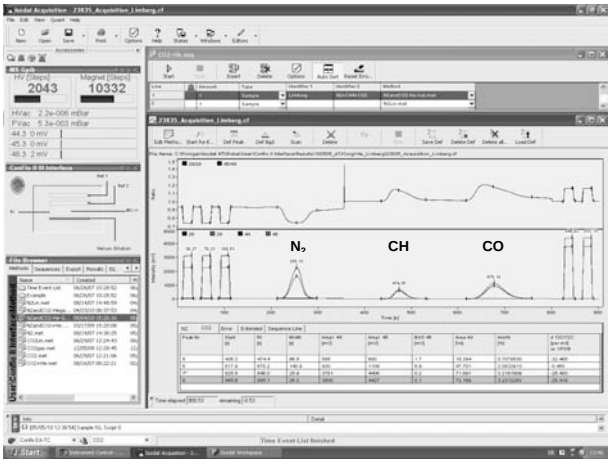

Fig. 2. Signal intensity trace of m/z 28 and 29 until 350 sec and 44 and 45 after of CH_4-CO_2-N_2-bearing fluid inclusions in quartz hosted by Jurassic sandstone (LSB, Germany)

The rapid high precision magnetic jump of the mass spectrometer, the injection of two different reference gases (N_2, CO_2), and the He-mode of the ConFlo III allow the simultaneous measurement of $\delta^{15}N$ and $\delta^{13}C$ of N_2, CH_4 and CO_2, respectively. The first three peaks shown in Fig. 2 are reference gas peaks for N_2, and the fourth peak is the N_2 peak of natural gas released from fluid inclusion by crushing. After jumping to the CO_2 option within 300 seconds, the CH_4 peak of the fluid inclusion gas appears well separated from the following CO_2 peak. The last two peaks are the reference gas peaks for CO_2 (Fig. 2). The intensity of the gas peaks, and the peak shape

indicate effective gas release and separation of N_2, CH_4, and CO_2. The complete gas separation and oxidation of CH_4 to CO_2 has been proven by multiple injections of gas mixtures with known isotopic compositions into the crusher followed by several blank measurements. The $\delta^{15}N$ and $\delta^{13}C(CH_4, CO_2)$ values of gases being released from fluid inclusions in individual chips of quartz from a sample site in the Lower Saxony Basin are shown in Table 1. The excellent reproducibility of $\delta^{13}C$ values for CH_4 and CO_2 indicates complete gas separation and oxidation of CH_4 to CO_2.

Sample	$\delta^{15}N$	$\delta^{13}C$ CH_4	$\delta^{13}C$ CO_2
Chip 1	-8.5	-33.6	-0.2
Chip 2	-6.9	-33.4	-0.8
Chip 3	-8.9	-32.9	-0.5
Chip 4	-7.9	-32.2	-0.3

Table. 1. ^{13}C and ^{15}N isotopic composition of fluid inclusions in quartz hosted by Jurassic sandstone (Lower Saxony Basin, Germany).

REFERENCES

Vonhof H.B., van Breukelen M., Postma O., RoweP.J., Tim C., Atkinson T.C., Kroon D.(2006) *Rap. Comm. Mass Spec.* 20: 25532558.