

Kinetic modeling of post-mature gas generation: Constraints from high-pressure thermal-cracking of $n\text{-C}_{24}$

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The formation of thermogenic gases in sedimentary basins is controlled by a series of cracking processes of organic matters. Gases formed directly from macromolecular precursors preserved in a source rock is termed as primary and those generated from oil (mainly hydrocarbons) cracking is termed as secondary. To date, little is known about the secondary wet gas cracking which might play a key role for some post mature gases where carbon isotopic reversal trend between the $C_1\text{-}C_4$ n -alkanes were occasionally found. It is widely accepted that organic matter cracking is mainly due to the temperature increase related to sediment burial, which is generally modeled by Arrhenius equations depending on temperature by an exponential law with kinetic parameters derived from laboratory pyrolysis experiments at higher temperatures. The influence of pressure is generally considered as a second-order factor compared to temperature and a few specific studies have reported the suppression of maturation with increasing pressure. Here pyrolytical studies were performed under high pressure and high temperature to constrain the inhibits of high-pressure on secondary wet gas cracking and further explore the late gas generation.

The pyrolyses were carried out in anhydrous closed system (gold tubes) for 24 hours under isothermal conditions (400°C and 430°C). The pressures range from 70 MPa to 700 MPa. A model compound, $n\text{-C}_{24}$, was chosen since it is present in any oil and less stable than short chain n -alkanes. The gas yields and carbon isotopes were measured and the rates of formation of the gas products were calculated.

Evidence for a high ^3He or low ^{10}Be production rate from cosmogenic nuclide cross-calibration

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An accurate knowledge on production rates is crucial for the precision of any application study of cosmogenic nuclides. However, current production rate uncertainties are at least 10-20%. For some nuclides (e.g. ^{21}Ne) experimental production rate determinations are rare, and model calculations often generate inconsistent results [e.g. 1]. Therefore, we have undertaken cross-calibration studies relating the production rates of ^3He , ^{10}Be and ^{21}Ne in various minerals to each other.

In a first study [2], the production rate of ^{10}Be (P_{10}) was calibrated against P_{21} in quartz from the Bishop Tuff ignimbrite, California. In spite of some erosion acting on that surface, a precise and robust value of $P_{10}/P_{21} = 0.245 \pm 0.008$ was obtained. Using $P_{10} = 5.0$ at $\text{g}^{-1} \text{a}^{-1}$ at sea level and high latitude ([3] with 2% muogenic contribution), this yields $P_{21}(\text{qz}) = 20.41 \pm 0.67$ at $\text{g}^{-1} \text{a}^{-1}$, in good agreement with the only experimental determination. Next, we compared ^3He and ^{21}Ne in olivine, pyroxene and quartz from the Bishop Tuff and from a basaltic andesite, which was sampled on the Puna plateau (Argentina) and contained a quartz xenocryst. A uniform $P_3(\text{ol,px})/P_{21}(\text{qz})$ ratio of 8.19 ± 0.19 was obtained, despite considerably different lithologies, sampling altitudes, and trapped He compositions. The comparison of ^{21}Ne in olivine, cpx, opx and quartz further enabled us to determine elemental production rates of $P_{21}(\text{Si}) = 43.7 \pm 1.4$, $P_{21}(\text{Mg}) = 203 \pm 13$, and $P_{21}(\text{Ca}) = 22 \pm 12$ at $\text{g}^{-1} \text{a}^{-1}$, when related to $P_{21}(\text{qz})$ as given above. However, the resulting $P_3(\text{ol,px})$ of 167.2 ± 6.7 at $\text{g}^{-1} \text{a}^{-1}$ is much higher than the “established” P_3 of ~ 115 at $\text{g}^{-1} \text{a}^{-1}$. Nevertheless, using our elemental P_{21} values in combination with the high P_3 yields very consistent exposure ages for independent olivine or pyroxene samples.

A wrong assessment of magmatic He or special production mechanisms (such as a significant ^3He production by thermal neutron capture of ^6Li) can be excluded for our samples. Therefore it seems that either $P_3(\text{ol,px})$ is much higher or $P_{10}(\text{qz})$ is much lower than established by direct experimental determinations.

[1] Niedermann *et al.* (2007) *EPSL* **257**, 596-608. [2] Goethals *et al.* (2009) *EPSL*, in revision. [3] Balco *et al.* (2008) *Quat. Geochron.* **3**, 174-195.