## A new strategy for identifying shales with high gas retention using noble gas, nitrogen and carbon

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Noble gases have been used to distinguish between hydrocarbon maturities, and evaluate the fracture network in a shale [1]. Carbon and nitrogen isotopic ratios, and noble gases, have the potential to identify the origin of shale gas. A combined study using all three simultaneously can strengthen previous applications, and have the potential of further utilizations. But such studies on shale gas cuttings are nonexistent.

The preferential adsorption of Xe and Kr is higher for kerogen than shales [2]. So, distinct fractionation pattern should set apart organic-rich shales. In conjunction with carbon and nitrogen isotopes, C/N and N/Ar ratios, they can provide useful insights on the type of sedimentary organic matter. A combination of stepwise combustion and vacuum crushing can be used to decouple the free and bound gases.

Acknowledgement: We thank the BG Group for a Research Grant 2013-17

[1] Hunt, Darah & Poreda (2012), *AAPG Bulletin* **96**, 1785-1811. [2] Prinzhofer (2013), *Noble Gases in Oil and Gas Accumulations* In: The Noble Gases as Geochemical Tracers Burnard P. (ed.) 225-248.

## A new analytical protocol for high precision EPMA of olivine

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Composition of olivine provides critical information on the composition and origin of primary mantle derived melts and their sources. Especially informative are minor and trace elements Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, Na [1, 2], which being in the concentration range over 10 ppm are assessable by EPMA.

Long counting times (up to 300 sec) on WDS at high beam current (300 nA) reported in [1] yield precision of individual analysis around 30 ppm (2 standard errors) for Ni, Mn, Ca, Al, Cr and 300 ppm for Fo content of olivine. Here we report 2-3 fold improvement of EPMA precision for larger range of trace elements in olivine (Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, Na).

The analytical protocol built up on brand new JEOL JXA 8230 EPMA in ISTerre, UJF, Grenoble, France. Facility has tungsten source gun, is equipped by five WDS and one SDD EDS and placed in the environment with controlled temperature (22+/-0.3 degrees C) and humidity (50+/-3%).

The analytical conditions are the following: acceleration voltage 25kV, 900 nA beam current, WDS recording for trace elements (Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, Na) and EDS recording for Si, Mg, Fe, total counting time 12 minutes, ZAF correction. Instrumental drift during analytical sessions is monitored by repeated measurements of olivine standards. For trace elements this protocol yields detection limits from 3 to 10 ppm and average precision of individual analysis of 10 ppm (2 standard errors). For Fo of olivine precision is 300 ppm (2 standard errors).

Comparison of EPMA and LA ICP-MS data for the large range of olivine compositions suggests that accuracy of EPMA is similar to precision noted above. For elements with concentration over 100 ppm the obtained EPMA precision and accuracy are better than these of LA ICP-MS. For the concentration of elements between 50-100 ppm both methods show similar precision and accuracy; and for concentration between 10-50 ppm LA ICP-MS yields better precision and accuracy. Spatial resolution of EPMA, however, is significantly better: 3-5 micrometres compared to 30-50 for LA ICP-MS. This makes our new EPMA protocol of great advantage for measurement of zoned or small olivine grains.

[1] Sobolev *et al.*, 2007. Science **316** (5823), p.412-417. [2] De Hoog *et al.*, 2010. Chemical Geology **270**, p. 196-2015