Migration of hydrocarbons recorded in calcite-hosted inclusions, Dead Sea area: trace elements and isotopic evidence

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The mechanisms of hydrocarbon (HC) migration with water fluids, as well as the ability of container minerals such as vein calcite to preserve HC geochemical tracers, have received much recent interest [1]. Calcitic veins enclosing HC and soot carbon have been discovered in the western side of the Dead Sea rift, where basin opening induced venting of water-methane fluids [2]. All veins share similar REE spectra defined by the calcite rare earths patterns. Calcite crystallized from solutions with seawater chemistry signatures [3]. The reconstructed water generation temperatures of 55-90°C fit the regional "oil window" located at the depths 2.5-4 km. Significant negative Ce/Ce* anomaly indicates calcite growth at high oxygen fugacity. The organic matter hosted by calcite has C:N:S ratios from 30:2:15 to 15:0.1:2 (in mole fraction) and contains abundant asphaltenes with trace amounts of alkanes and carbonyl groups. Measured values $\delta^{13}C_{org}$ (–26.9 to –27.2 ‰ PDB) and $\delta^{34}S$ (+5.5 ‰ CDT) are similar to those of the Dead Sea asphaltenes [4]. As the obtained data imply, the calcite veins with inclusions of both oxidized and biodegraded HC and soot carbon precipitated from Ca-Na-HCO_3-Cl sediment waters that entrained crude oil drops.

[1] Rongxi *et al*. (2011) *Rus. Geol.Geoph*. **52**, 1491-1503. [2] Gvirtzman & Stanislavsky (2000) *Basin Research* **12**, 79-93. [3] Bau & Dulski (1996) *Precamb. Res*. **79**, 37-55. [4] Nissenbaum & Goldberg (1980) *Org. Geochem*. **2**, 167-180.

Gramaccioliite-(Y) – rare yttrium carrier in metamorphic rocks (Subpolar Urals, Russia)

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Gramaccioliite-(Y) is related to crichtonite group which includes the series of complex titanium and iron oxides with general formula $ABC_{18}T_2O_{38}$, where A = Sr, Pb, Ca, Na, R, REE, Ba, U; B = Mn, Y, REE, U, Zr; C = Ti, Fe^{3+}, Cr и T = Fe^{3+}, Mg. For the first time it was found in biotite gneisses of Piedmont province (Italy) and named in honor of Professor of Milan University Carlo Maria Gramaccioli [1]. We found gramaccioliite-(Y) on Maldynyrd Ridge (Subpolar Urals) in hematite-sericite shales. This is the first find in Russia. The mineral was found as well composed tabular crystals with trigonal habit with rhombohedral side planes, with black coloring and metal shine. In association with it we found leucoxene, rutile, anatase, apatite, cyanite, epidote, garnet, tourmaline, monazite and fuchsite, gold in important quantities. Gramaccioliite-(Y) was studied with scanning electron microscope JSM-6400 with energy spectrometer Link. The calculated empirical formulas of gramaccioliite-(Y) are as follows:

$(Pb_{0.61}Sr_{0.27}Ba_{0.02}U_{0.02})_{0.93}(Y_{0.49}Mn_{0.37}Ce_{0.08}Ca_{0.04}Nd_{0.02}La_{0.02})_{1.01}\times(Ti_{13.53}Fe_{5.49}Zn_{0.22}V_{0.04}Nb_{0.04})_{19.33}O_{38}$ [1].

$(Pb_{0.60}Sr_{0.39})_{0.99}(Y_{0.55}Mn_{0.42})_{0.97}(Ti_{13.32}Fe_{6.01}Zn_{0.53}V_{0.18})_{20.04}O_{38}$ – our data.

It is noticeable that the mineral, discovered by us, differs from the one, discovered in Italy, by considerably lower quantity of impurities, and its formula is practically identical to approved one (IMA 2001–034): $(Pb,Sr)(Y,Mn)(Ti,Fe)_{18}Fe_2O_{38}$ [1]. The formation of gramaccioliite-(Y) is conditioned by geochemical and mineralogical features of metamorphized rocks, formed on Precambrian substrate of contrasting content and modified by hypergenic processes. On the one hand the high titanium content of basites, presence of lead and zinc as galenite and sphalerite inclusions, on the other hand – rare earth and manganese anomaly, which is characteristic for rhyolites of this region – all these were favorable formation factors for complex titanium and iron oxide - gramaccioliite-(Y).

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[1] Orlandi P.et al/ (2004) *European Journal of Mineralogy* **16**, 171–175.

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