

## EA-IRMS: Analysis of graphite and diamond

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The continuous-flow mass-spectrometry with EA + ConFloIII is widely used for the isotop analysis of organic carbon, oil fractions, coals, kerogens and doesn't use for measurement of carbon isotope ratios in graphites and diamonds.

The theoretical precondition of complexity of the isotope analysis of graphite is connected with the increase of order strength in graphite structure from amorphous to hexagonal form and, accordingly, with growth of activation energy for the reaction of carbons nanocluster oxidation using molecular oxygen. It is interesting, that in contrast to the oxidation of amorphous and linear particles of carbon at which formed only CO<sub>2</sub> molecules, in grafen clusters oxidation CO<sub>2</sub> as well as CO may be formed. All these factors finally lead to incomplete combustion of graphite using standard EA-IRMS technique.

Moreover, there is a problem of isotopse zonality of carbon and heterogeneity in diamond crystal. Our experiments have shown, that the <sup>13</sup>C/<sup>12</sup>C ratio of various domains of a diamond crystal can vary within the limits of 0.5-3 ‰. The typical picture of a diamond crystal burning is presented in the table.

№ of sample	№ of a oxygen portion				
	1	2	3	4	5
	$\delta^{13}\text{C}, \text{‰}$				
1	-14,9	-13,9	-14,3	-14,4	-14,7
2	-6,0	-4,3	-4,5	-4,7	-5,2

The technique used for analysis of <sup>13</sup>C/<sup>12</sup>C in graphites and diamond is an adaption of continuous-flow mass-spectrometry with EA + ConFloIII methods that used for the <sup>13</sup>C/<sup>12</sup>C ratio determination in organic compounds.

In our experiments we used submission of several oxygen portions. The temperature of an oxidizing reactor in EA was 1020°C. Molybdenum and tungsten oxides are added do the investigated sample in order do achieve complete combustion.

### Reference

Zavodinsky, V.G. Computer investigation of carbon nanaclusters and their activities in reactions with molecular oxygen (2004) *Phys. of low-dimensional structures*. 35-48.

## Experimental study on the mechanism of metasomatism in the system between scheelite and huebnerite

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Experiments on metasomatism were carried out in the tungstates (scheelite and huebnerite) - aqueous solutions (MnCl<sub>2</sub> and CaCl<sub>2</sub>) system. We changed duration (1.5 to 1440 hours), concentration of aqueous solution (0.01, 0.1, 1.0 mol/l) and temperature (100 to 170°C) systematically. Reaction mechanism was considered based on the observation of the mineral texture and chemical analysis of experimental solutions.

In the scheelite - MnCl<sub>2</sub> system, huebnerite crystals grow toward the inside of host scheelite accompanying a lot of void space. The texture is categorized into pseudomorphic replacement texture. However, in the huebnerite - CaCl<sub>2</sub> system, small amount of scheelite was precipitated on the surface of host huebnerite. The texture is categorized into rim replacement texture. Since molar volume of huebnerite (41.88 cm<sup>3</sup>) is smaller than that of scheelite (47.05 cm<sup>3</sup>), the reaction solution can easily penetrate through the reaction layer to reach the unreacted scheelite in the former system. The progress of the replacement inside the host mineral is dependent on the ratios of the morecular volumes of the minerals. This is why the replacement textures are different in two systems. In the former system, dissolution of the starting material was a rate limiting process. And, in the latter system, precipitation of the product was probably a rate limiting process.

Dissolution rates of scheelite and huebnerite were obtained from the changes in concentration of the solution which was obtained from the dissolution of the product. Activation energies in the three different concentrations (0.01, 0.1, 1.0) were calculated. Activation energies of scheelite dissolution were estimated to be 16.6×10<sup>-3</sup>, 18.5×10<sup>-3</sup> and 16.9×10<sup>-3</sup> kJ/mol for 0.01, 0.1 and 1.0 mol/l aqueous MnCl<sub>2</sub> solution respectively. Activation energies of scheelite dissolution were estimated to be 1.5×10<sup>-4</sup>, 18.0×10<sup>-4</sup> and 18.5×10<sup>-4</sup> kJ/mol for 0.01, 0.1 and 1.0 mol/l aqueous CaCl<sub>2</sub> solution respectively. The former values were about one order of magnitude larger than the latter.