

Hg and CH₃Hg mass balances for the Venice Lagoon (Italy)

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The Venice Lagoon is a large (549 km²), shallow (≈1.0 m) enclosed embayment located on the northwestern Adriatic Sea. The lagoon was contaminated with more than 50,000 Kg of mercury from chlor-alkali plants which operated without pollution control from 1951-1986. As part of a biogeochemical assessment, Hg and CH₃Hg were measured seasonally throughout 2002 in the sediments, water column, suspended matter, rivers and rainfall at 10-15 locations. These data are the first ever collected from this lagoon using ultra-clean sampling and analytical protocols. Mercury speciation was determined using cold vapour atomic fluorescence spectrometry (CVAFS). Concentration data were converted to fluxes using historic literature values for mass flows of water, suspended matter, rainfall, etc. As indicated in the table, approximately 2,000 Kg of Hg per year cycle through the lagoon, most of it as a result of the resuspension of historically contaminated bottom sediments. Sediments are readily resuspended by both wave action and anthropogenic activities, and then transported to the Adriatic Sea by tidal flushing. Approximately three times as much CH₃Hg was estimated to enter the lagoon, compared to the amount that exits. This difference may be due to photochemical or biotic demethylation, although no measurements of these rates has yet been undertaken.

INPUTS	Total Hg		Methyl Hg	
	Kg/yr	%	Kg/yr	%
precipitation	7.2	0.4	0.001	0.003
rivers	19.8	1.0	0.16	0.5
industry	36.0	1.8	0.36	1.2
Adriatic Sea	308	15.0	2.4	8.1
porewater	25	1.2	25	84.5
city canals	5.8	0.3	0.16	0.5
resuspension	1,649	80.4	1.5	5.1
SUM IN	2,051		29.6	

OUTPUTS	Total Hg		Methyl Hg	
	Kg/yr	%	Kg/yr	%
Adriatic Sea	1,800	99.8	9.7	97.9
fishing	0.22	0.01	0.21	2.1
atmosphere	4.2	0.2	0.001	0.001
SUM OUT	1,804		9.9	

The role of sulfide medium in diamond crystallization: experiments at 6-8 GPa

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Sulfide minerals are quite abundant in the diamond assemblage and they are met as inclusions in diamond crystals – pyrrhotite (Po), pentlandite (Pn), monosulfide solid solution (Mss) – and mantle xenoliths of peridotitic (Pn, Po) and eclogitic (Po, pyrite (Py), Cu-sulfides) types. The diversity in sulfide composition of mantle rocks results from their long evolution and such processes as mantle metasomatism, that leads to the enrichment of initial sulfides in Cu, K, Cl. Because of this, initial sulfide mantle mineralization is perfectly presented only by inclusions in diamonds.

Our experiments were conducted in an anvil-with-hole apparatus with a cell made of lithographic stone, graphite ampoule-heater, and testing diamond seed – monocrystal with a size of 0.5–0.6 mm grown in Ni–Mn–C melt. The pressure of 6–8 GPa was maintained with an accuracy of ±0.1 GPa.

Crystallization of diamond at high pressures of 6–8 GPa in sulfide-carbon melts occurred in octahedral habit and was quite rapid (during the first 1–2 min from the beginning of spontaneous nucleation). The growth of layers of the newly formed "sulfide" diamond was also observed on the seeds. According to the textural signs, sulfide phases during the diamond synthesis were in the state of homogeneous melt, but crystallized at the last stage of the experiment during the decrease of temperature under high pressure. Depending on the starting materials sulfides were represented by mixtures of Ccp and Po, Ccp and Pn without any signs of decomposition and formation of native metals (i. e. there were no metal-carbon melts that could dissolve carbon during recrystallization of graphite to diamond). In our experiments graphite was most likely dissolved in sulfide melts and, as a result, sulfide-carbon melts with high contents of dissolved carbon were formed.

Thus the role of sulfide melts in the diamond formation was demonstrated experimentally on the base of natural sulfide inclusions in diamonds. This role was also illustrated in our experiments on diamond synthesis in the presence of covellite (CuS) and argentite (Ag₂S) that do not contain Fe and Ni – so-called "catalysts" of diamond synthesis. It means that the "sulfide version" of the diamond genesis must be also considered together with the traditional carbonate model.

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