

## <sup>129</sup>I dating of hydrocarbons in gas hydrate deposit, off Shimokita Peninsula, Japan

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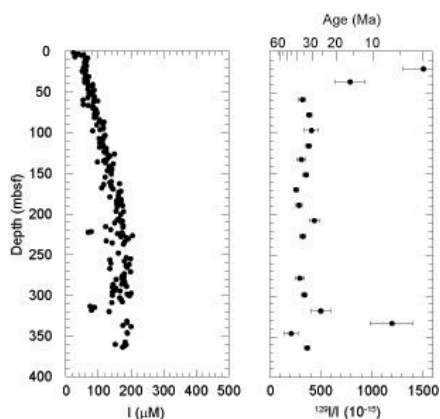
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### <sup>129</sup>I Geochronology

Natural iodine system comprises one long-lived radioactive iodine (<sup>129</sup>I;  $T_{1/2}=15.7$  Myr) as well as stable <sup>127</sup>I. Because of the strong biophilic behavior of iodine, marine organic materials are enriched in iodine, and the subsequent decomposition of buried organic materials liberates iodine into pore waters together with hydrocarbons. The <sup>129</sup>I/I measurements in pore waters thus provide the collapse time since the organic materials had accumulated and separated from seawater. Here we show the <sup>129</sup>I/I results from the gas hydrate deposits off Shimokita Peninsula, NE Japan to determine the source formations responsible for hydrocarbons in gas hydrate.

### Results and Discussion

Iodine concentrations rapidly increase downward, reflecting upward migration of deep fluids enriched in iodine. The <sup>129</sup>I/I ratios range between  $300 \times 10^{-15}$  and  $400 \times 10^{-15}$ , suggesting ages for iodine and hydrocarbon sources as old as 40 Ma. These ages correlate well with the Eocene coaly formations, which are also responsible for the conventional natural gas deposit underlying the gas hydrate.



## Importance of soil organic matter to sorption of insecticidal Cry proteins

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We have developed a theoretical framework that describes the influence of soil organic matter on the fate of insecticidal Cry proteins from genetically modified *Bt* crops in agricultural soils. We performed in situ monitoring of protein adsorption to and desorption from various humic acids (HA) at different solution conditions (pH, ionic strength) using a quartz crystal microbalance (QCM-D). We reproducibly coated HA to QCM-D sensors via electrostatic layer-by-layer assembly (SiO<sub>2</sub>—poly-L-lysine—HA). We investigated adsorption of Cry1Ab to a variety of HA that differ in chemical composition and origin. These different materials showed a remarkably similar pH and ionic strength dependence of Cry1Ab adsorption. From a modeling standpoint, these results suggest that sorption of Cry proteins to different soil organic matter types may be captured by one set of parameters. The adsorbed concentration of Cry1Ab to HA decreased slightly with increasing pH, and, in contrast to hydrophilic and negatively charged quartz, the initial adsorption rate of Cry1Ab to HA was independent of solution pH. These findings imply that Cry-HA interactions are governed by hydrophobic and/or entropic interactions, while electrostatics have a minor modulating effect. This was corroborated in control experiments in which adsorption of Cry1Ab to negatively charged poly-acrylic acid was highly pH dependent and, hence, governed by electrostatics. A significant mass fraction (70-80% at pH 5 and 6 and 50-70% at pH 7 and 8) of Cry1Ab adsorbed to HA did not readily desorb upon buffer rinsing, indicating that the protein may have partially unfolded on the HA surface. Therefore, in field soils, much less Cry is expected to desorb from HA than from mineral surfaces upon decreasing protein solution concentrations. Our results indicate that soil organic matter is an important sorbent for Cry proteins and that its relative contribution to total adsorption increases with pH as adsorption to negatively charged minerals decreases.