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Gas hydrates and magnetism: comparative geological settings for diagenetic analysis

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ABSTRACT

Geochemical processes associated with gas hydrate formation lead to the growth of iron sulphides which have a geophysically-measurable magnetic signature. Detailed magnetic investigation, complemented by petrological observations, were undertaken on cores from a permafrost setting, the Mackenzie Delta (Canadian Northwest Territories) Mallik region, and two marine settings, IODP Expedition 311 cores from the Cascadia margin off Vancouver Island and the Indian National Gas Hydrate Program Expedition 1 from the Bengal Fan. Stratigraphic profiles of the fine scale variations in bulk magnetic measurements correspond to changes in lithology, grain size and pore fluid geochemistry which can be correlated on local to regional scales. The lowest values of magnetic susceptibility are observed where iron has been reduced to paramagnetic pyrite, formed in settings with high methane and sulphate or sulphide flux, such as at methane vents. High magnetic susceptibility values are observed in sediments which contain detrital magnetite, for example from glacial deposits, which has survived diagenesis. Other high magnetic susceptibility values are observed in sediments in which the ferrimagnetic iron-sulphide minerals greigite or smythite have been diagenetically introduced. These minerals are mostly found outside the sediments which host gas hydrate. The mineral textures and compositions indicate rapid disequilibrium crystallization. The unique physical and geochemical properties of the environments where gas hydrates form, including the availability of methane to fuel microbiological activity and the concentration of pore water solutes during gas hydrate formation, lead to iron sulphide precipitation from solute-rich brines. Magnetic surveying techniques help delineate anomalies related to gas hydrate deposits and the diagenesis of magnetic iron minerals related to their formation. Detailed core logging measurements and laboratory analyses of magnetic properties provide direct ties to original lithology, petrophysical properties and diagenesis caused by gas hydrate formation.

Keywords: gas hydrates, magnetism, solute exclusion, iron-sulphides, Mallik, Cascadia Margin, Bay of Bengal, sediments

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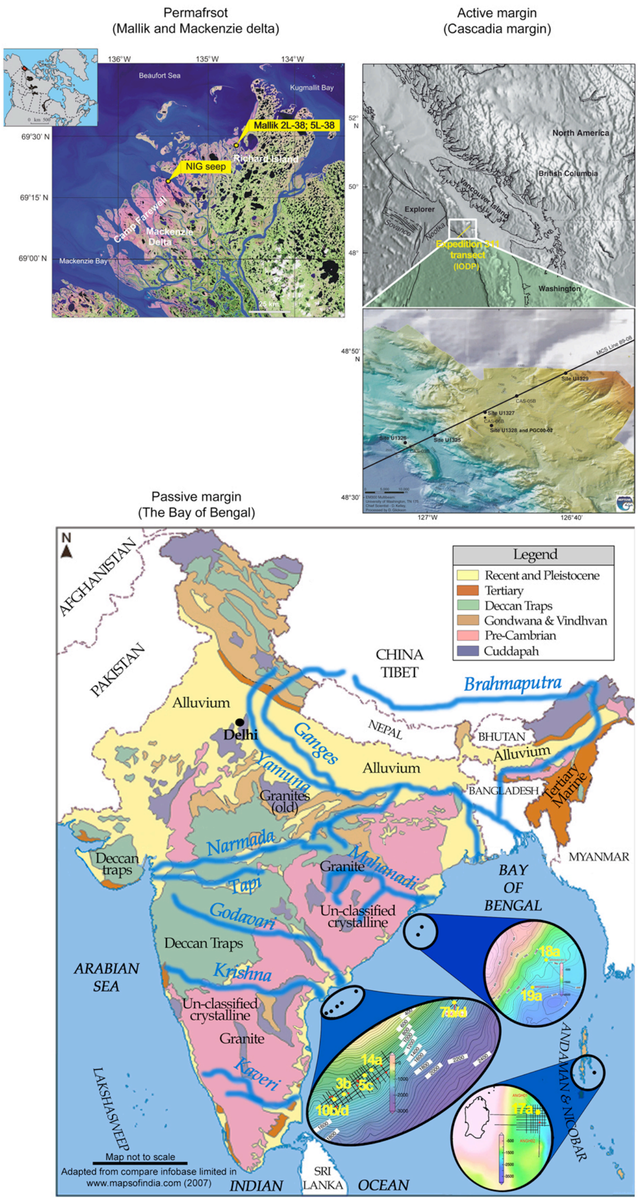

Figure 1: Location of the three regions which have been cored, sampled and magnetically studied. One site in permafrost at Mallik, 5 sites in the active margin (marine offshore) in the Cascadia Margin and 8 sites in the Bay of Bengal basin in a passive margin.

Introduction

Geophysical and geochemical methods have become increasingly utilized over the last 40 years to locate and quantify natural gas hydrate deposits and to better understand these resources, their climate impacts and their potential role in geohazards.

In order to understand the mechanisms of gas hydrate formation and its natural distribution in sediments, magnetic methods have been used on cores from three different geological settings (Fig. 1). At Mallik (Northwest Territories, Canada), the gas hydrates occur in Tertiary fluvial sediments of the Mackenzie delta which have been affected by deep, multi-ice age permafrost. On the Cascadia active margin west of Vancouver Island (British Columbia, Canada), the gas hydrates are hosted in Quaternary diamicts and older Tertiary bathyal marine sediments of the deformed accretionary wedge. In the Bay of Bengal (Indian Ocean), the gas hydrate deposits are formed in an extensive Tertiary to Recent passive margin sequence of foredeep terrigenous clastic sediments and bathyal marine hemipelagic muds.

Magnetic methods are rapid and able to distinguish and resolve the detrital contribution from ferrimagnetic iron oxides, usually magnetite and hematite, relative to the authigenic contribution carried by ferrimagnetic iron sulphide minerals, typically greigite and smythite. Both contributions have their magnetic concentration, grain size and mineralogy influenced by geological setting and history, in particular the thermal and fluid sequence for the formation and dissociation of gas hydrates.

Sediment bulk composition, its grain size distribution and porosity/permeability control not only the distribution of gas hydrate but also the availability of pore fluids and soluble ions, including iron, which react or precipitate as new diagenetic minerals. The paragenesis usually results in the formation of iron sulphides, carbonates and clays. The compositions and textures of these new minerals are controlled by the gas hydrate crystallization process, brine composition, methane flux and the presence of methanotropic bacteria, in a reducing environment. These diagenetic changes serve to cement the sediment and to introduce new magnetic signals.

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The magnetic results combined with petrological, geochemical, and both borehole and core sample geophysical data serve to discriminate the influence of gas hydrate on the diagenetic magnetic signal in these different geological settings and provide the basis for a general model to explain gas hydrate formation, distribution and diagenesis.

Permafrost setting: Mallik and the Mackenzie Delta

The Mallik deposit (Fig. 1), has been magnetically studied in the JAPEX/JNOC/GSC gas hydrate program by aeromagnetic mapping of the Mackenzie delta and core logging of magnetic susceptibility [1] and detailed sampling for specialized laboratory bulk magnetic properties [2].

Aeromagnetic mapping

The Mallik gas hydrate deposit is near a sub-oval magnetic high, oriented NW-SE (7.5 km long and 3-4 km wide) revealed by filtering out long wavelength regional trends (Fig. 2a). The outline corresponds to reflection-seismically imaged faults [3]. Magnetic modelling shows that the source of this magnetic high lies in the upper 1250m, suggesting the cause for the magnetisation coincides with the known spatial and stratigraphic distribution of the gas hydrate and permafrost at Mallik. The hypothesis that strong diagenetic magnetic signal related to gas hydrate formation provides a causal mechanism to explain the magnetic anomaly motivated the present study.

Mallik Core results

To verify the magnetic body model from aeromagnetic data, a 220 m interval of core (well 5L-38) from 885 m to 1152 m depth in the Mackenzie delta was sampled through alternating fluvial-deltaic silt and sand layers. The gas hydrates preferentially occur in quartz sand horizons, infilling about 50-90% of the ~35% porosity. Strong contrasts of the magnetic susceptibility appeared between sand and silt lithologies with the highest intensity being found in the silt horizons (Fig. 2b). Magnetic hysteresis and remanence measurements have shown the lowest saturation (M_S), the highest coercive force (H_C) and the finest magnetic grain size (M_{RS}/k) in sand infilled with at least 80% gas hydrates.

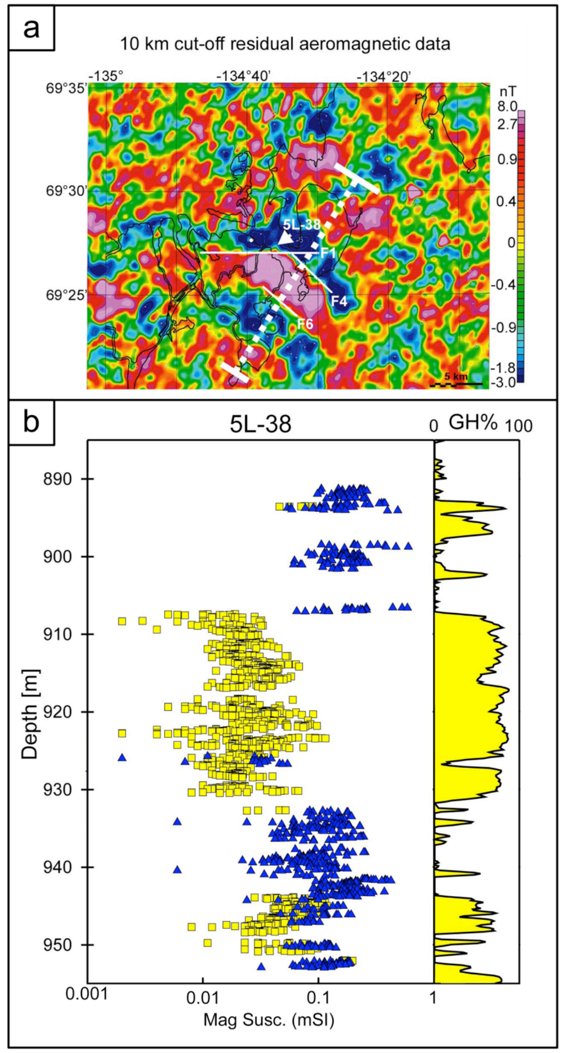

Figure 2: Magnetic investigations at Mallik (Northwest Territories of Canada): a) Aeromagnetic map after 10 km cut-off residual magnetic intensity showing positive magnetic anomaly bounded by offset faults; b) magnetic susceptibility measurements in the core 5L-38 compared with the well-log gas hydrate concentration (%), with silt-layers marked with blue triangles and sand-layers marked with yellow squares.

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Petrographic and Geochemical results

Some samples were prepared as thin sections to be observed by reflected and transmitted optical microscopy. The sediments comprise quartz, arenite sands and sublithic quartz arenite silts where the lithic component is often chert and quartz rich metasediments. Detrital magnetites are the most abundant primary magnetic mineral but cements are dominated by pyrite, often rich in manganese. This pyrite occurs with dolomite and Mn-calcite in filled tensional veins and fractures which cross cut primary detrital sand and silt grains and inflate the matrix from the pore volume with bacterial textures. Magnetites in the same sections are unaltered and often overgrown by massive diagenetic iron-sulphides.

This demonstrates that magnetite alteration in the gas hydrate stability field is not the source for the iron in the diagenetic cements. Due to the relatively pure quartz-rich composition, other siliclastic grains are an unlikely source for the Fe^{2+}, Mn^{2+}, S^{2-} and CO_4^{-2} ions.

Discussion

The magnetic properties combined with optical observations and chemistry suggests that authigenic iron-sulphide growth occurs preferentially in the silts, away from sand horizons filled by gas hydrates, by solute exclusion. The gas hydrate crystallisation selectively takes up much of the pore water from the pore space, expelling all of the dissolved ions as a brine into the adjacent, less permeable silt layers. These adjacent layers have been intensely cemented, fractured and inflated with authigenic carbonates and iron sulphides with bacterial textures, coinciding with high susceptibilities due to ferrimagnetic greigite or smythite among the diagenetic iron-sulphide cements.

Active margin setting: Cascadia margin

The Cascadia accretionary wedge west of Vancouver Island (Fig. 1) is composed of Tertiary terrigeneous and hemipelagic sediments, pre-Pleistocene and Pleistocene hemipelagic clayey to silty sediments overlain by Late Pleistocene-Early Holocene glacial diamict. These sediments were first investigated by a transect of several shallow sediment cores crossing a methane seep over a BSR. Subsequently, they were sampled at 5 sites from ODP leg 146 and IODP expedition 311.

Sediments from seafloor above a seep methane chimney

A transect of 2-8m long sediment cores across the Bullseye methane vent and gas hydrate deposit was undertaken, and magnetic susceptibility was logged [4]. Outside of the vent, the magnetic susceptibility ranges from 2000 to 4000 µSI and decrease inside the vent to as low as 50 µSI in the center. Physical core descriptions revealed a high concentration of authigenic pyrite inside the vent whereas abundant detrital magnetites occur with little pyrite outside the vent. The high methane flux provides enough energy or food source for sulphate reducing bacteria using in the pore water to reduce the sulfur and synthetize pyrite.

Deep cores transect: magnetic results

5 sites (U1325 to U1329) have been sampled every 50 cm depth during Expedition 311 (IODP) for a total of 1692 discrete samples to measure stratigraphic variation of bulk magnetic properties (Fig. 3). In the Pleistocene section, magnetic susceptibility is bimodal with one mode at 200 µSI (dominated by diagenetic iron-sulphides) and the other one at 2000 µSI, dominated by detrital magnetites from dropstone deposits and masking any iron-sulphide signal. The detrital magnetic signal is only observed on the top 150 mbsf in sites 1325, 1327 and 1328. The lower part of these sites and 1329 have low magnetic susceptibilities as expected for the typical reducing environment for pyrite-bearing marine sediments.

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Nevertheless, these low values are punctuated by some clay-rich layers with higher susceptibility values, especially in the middle of these bands. These clay layers are characterized by fine magnetic grain size ($D_{JH} > 0.1$ where D_{JH}= $[M_{RS}/M_S]/[H_{CR}/H_C]$; [5]) and the occurrence of ferrimagnetic iron-sulphides as indicated by M_{RS}/k [6], the shape of the curve of thermomagnetic remanence and susceptibility with their characters which change at ~325°C.

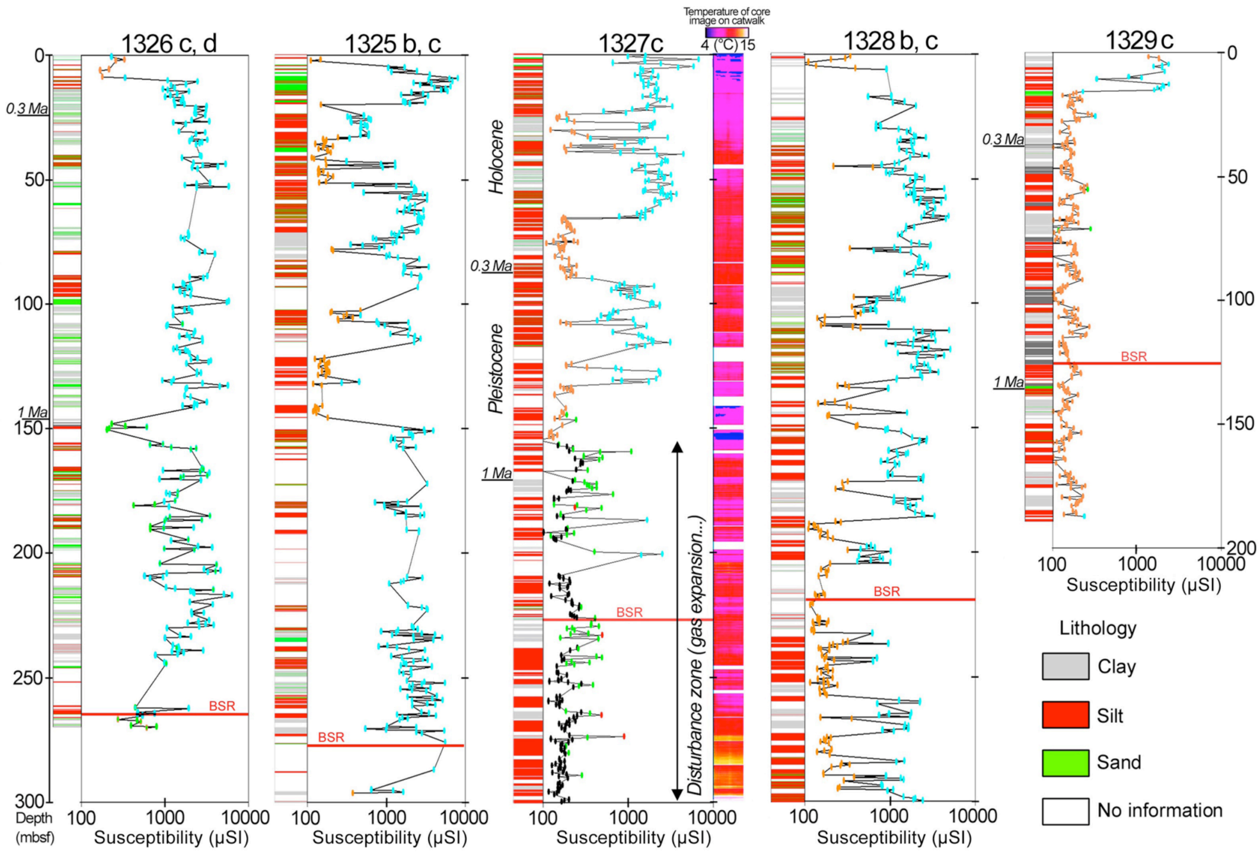

Figure 3: Logs of lithology and magnetic susceptibility with depth across the IODP Exp311 transect of the Cascadia margin (Canada). The color of magnetic susceptibility dots represents an intensity scale: orange for very low susceptibility and blue for high susceptibility in levels influenced by dropstone deposits. Black, green and red also mark an increase of magnetic suceptibility but for the lower part of U1327 subjected to diagenesis perturbation by gas hydrates. The infra-red thermal log for U1327 is compared to show gas hydrate concentrations.

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Optical observations

Large detrital magnetites, without any alteration rims, dominate dropstone deposits while framboidal pyrite often deposited along curveplanar bacterial films dominate outside of the dropstone layers (Fig. 4). In the top 150 mbsf, pyrite cements inflate and raft apart coarse silts. Below 150 mbsf, coalesced needles or clusters of blades of greigite/smythite (Fig. 4d) are common from 20 µm down to suboptical sizes. Bulk magnetic measurements are dominated by single domain magnetic grain sizes (i.e. < 0.1 µm) with gas hydrate crystallisation.

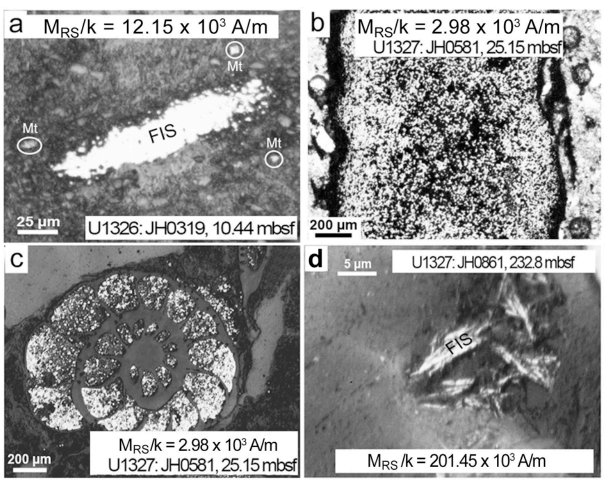

Figure 4: Transmitted-reflected optical observations in representative samples from Cascadia margin. a) silty sample with detrital magnetites (Mt) cut by veins of ferrimagnetic iron-sulphides (FIS); b) big veins of greigite with bacterial texture, c) fossil totally filled by iron-sulphides grains; d) coalesced needles of greigite or ferrimagnetic iron-sulphides in clay layers.

Discussion

As in the permafrost setting, the solute exclusion mechanism apparently controls diagenesis in these marine deposits. The marine muds of the Cascadia accretionary wedge differ from the sands and silts of the Mackenzie/Beaufort basin by more primary detrital magnetite and nearly modern marine pore water composition. The needle and bladed texture of ferrimagnetic iron-sulphides calls for a rapid brine concentration and fluid exclusion from gas hydrate levels, forcing of the greigite and smythite precipitation to slower diffusion controlled. Clay layers around gas hydrates seem to act as sponges leading to greigite/smythite precipitation driven by bacteria from saturated solutions activity in the presence of high methane flux.

Passive margin setting: the Bay of Bengal

Three regions in the National Gas Hydrate Program of India (NGHP, Exp-01) were drilled in the Bay of Bengal (Fig. 1). All cores were logged and sampled every 150 cm (1 per section): including a transect of 5 holes in Krishna-Godavari basin (KGB), 2 in Mahanadi basin (MB) and 1 in the western part of Andaman Islands basin (AIB), to obtain a collection of 990 samples. Sediments from KGB and MB are fluvio-deltaic and turbidite susccessions deposited of the east coasts of India since Eocene-Oligocene. By way of contrast, AIB has only a distal turbidite susccession from Eocene-Oligocene and overlain by Miocene-Pliocene clayey hemipelagic sediments.

Magnetic results

High values of magnetic susceptibility and remanence are observed throughout the collection attributed to coarse-grained detrital magnetites derived from continental rivers, particularly in KGB where the provenance of terrigeneous sediment supply was more efficient (Fig. 5; light blue layers). These routinely high magnetic susceptibility values are punctuated by peaks of very high values (dark blue layers) corresponding to intense and short duration detrital events such as flooding, tempestites and tsunami deposits.

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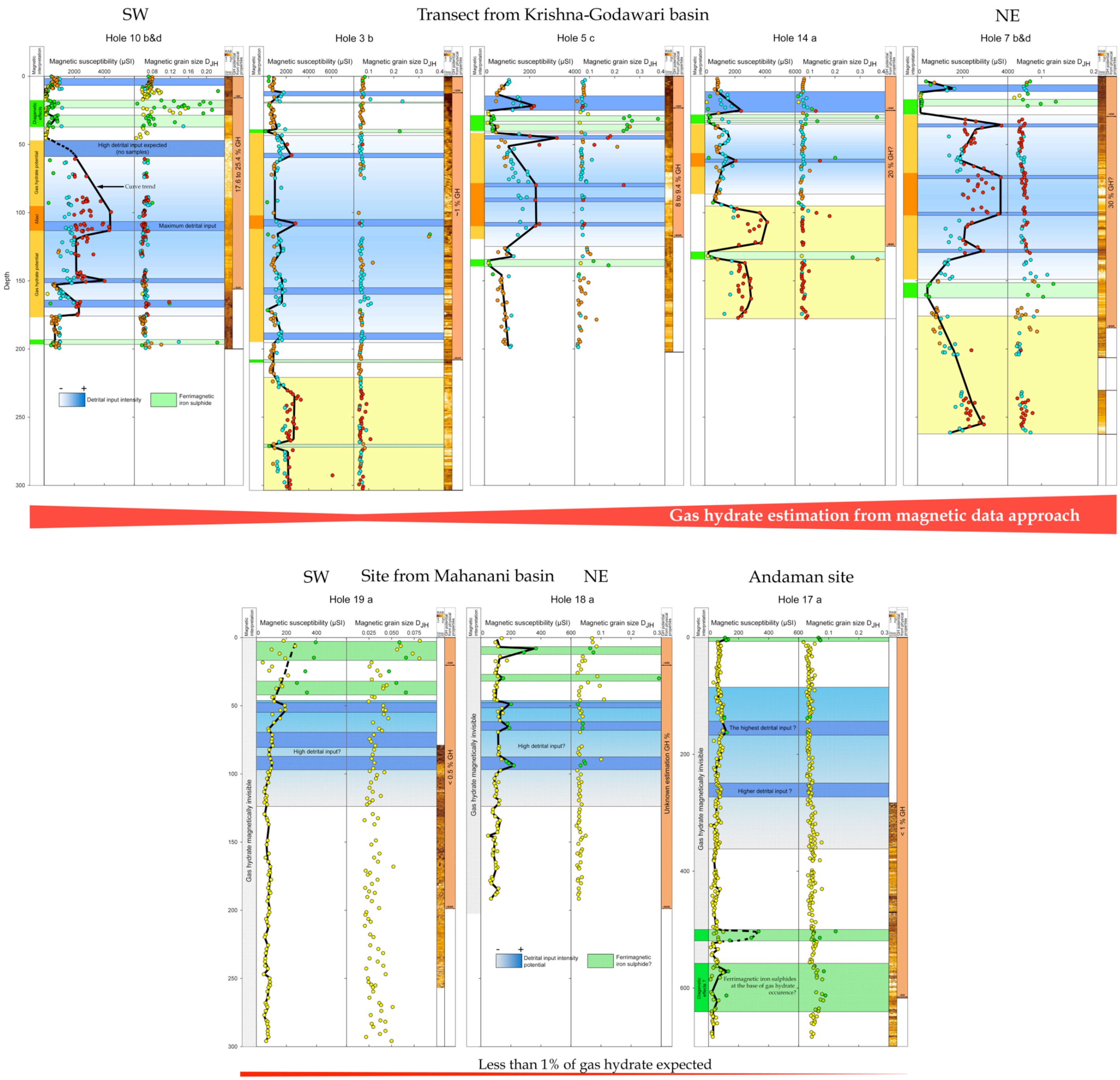

Figure 5: Magnetic comparison with depth between each site from the Bay of Bengal basin. Magnetic susceptibility and grain size (D_{JH}) are compared with resistivity at bit logs (RAB) for gas hydrate location. The color of data represents the magnetic susceptibility scale used to separate different behaviour and help to create a proxy for gas hydrate occurrence and concentration. Some correlations are proposed: blue layers for detrital signal, green layers for diagenetic signal from gas hydrate effects and yellow layers for other detrital signal.

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The high mean susceptibility value is linearly correlated to the site-mean gas hydrate concentration, allowing the magnetic measurement to be used as a proxy and to provide a rough calibration of gas hydrate content.

The gas hydrate zones are bracketed by clay-rich layers (Fig. 5; green layers), subjected to intense diagenesis, where fine grained ferrimagnetic iron-sulphides (greigite/smythite) are produced [k = 150-300 μSI] and $D_{JH} > 0.1$.

This diagenesis took place under high concentrations of salinity and alkalinity, especially for sulphate reduction and bicarbonate production related to bacterial activity. Thermomagnetic decay curves and optical petrographic observations confirm this analysis.

These magnetic behaviours are correlatable within-basin and between the basins allowing sea levels and climatic interpretations from the detrital signal in the Bay of Bengal during the Quaternary period.

General Discussion and Model

Comparison of magnetic susceptibility with magnetic grain size (D_{JH}) between different geological settings provides an excellent method to discriminate gas hydrate occurrence, or more precisely, the effects of gas hydrates on the sediments (Fig. 6). These measurements reveal the control of magnetic heterogeneities due to primary variation in the sedimentary deposits as well as diagenetic effects attributed to gas hydrate formation [7].

In the Indian Ocean settings, layers of coarse detrital sediments serve to localize the gas hydrate deposits. A marked diagenetic signal of magnetic susceptibility, k from 150 to 300 μSI and D_{JH} > 0.1, highlights the fine grains of greigite/smythite which are found at the edges of the gas hydrate layers. This is particularly evident in clayey layers or in the layers with the lowest permeability, where freezing and volume expansion related to gas hydrate formation creates local fractures (Simplified model, Fig. 7).

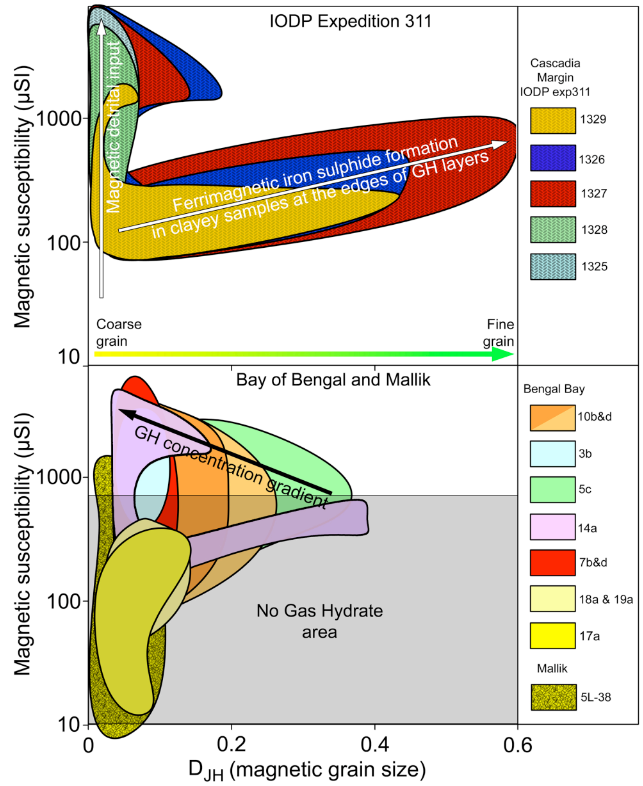

Figure 6: Magnetic susceptibility compared with magnetic grain size (D_{JH}) in all the three sites. Contour are plotted between each well-core population to discriminate the effect of gas hydrate on the position of the population and the effect of the geological settings (permafrost, active and passive margin).

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Concentrated brines formed and migrated suddenly when the gas hydrate froze, expelling solutes into neighbouring layers and the fractures which cut them.

The brines, and the inflationary space they occupy, collect methane and create an environment favourable to bacteria which feed on the high methane flux. Methane oxidation produces electrons which reduce minerals such as iron oxides and sulphides when they receive new electrons. Without low permeability layers, the fluid migration diffuses throughout all of the formations above the BSR leading to complete pyritisation without preserving the ephemeral ferrimagnetic iron sulphide signal.

The magnetic properties of gas hydrate bearing sediments is thus a combination of the original detrital content and the diagenetic transformations of iron minerals caused by the unique environment gas hydrate formation produces. The availability of methane to provide food for bacteria coupled with the concentration of solutes outside gas hydrate accumulation zones leads to the creation of iron sulphides. These new minerals are observable using magnetic techniques, which help in delineating the gas hydrate formation mechanism and may be developed into new geophysical methods of gas hydrate exploration.

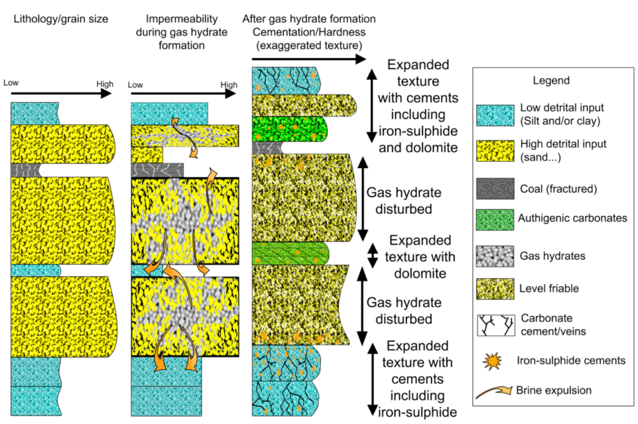

Figure 7: Model of diagenesis perturbed by gas hydrate in Mallik 5L-38 well-core.

References

[1] Lowe, C., Enkin, R.J., Baker, J. and Dallimore, S.R. *Investigation of airborne magnetic data and magnetic properties of cored rocks from the Mallik gas hydrate field. In: Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada, (ed) S.R. Dallimore and T.S. Collett*. Geological Survey of Canada, 2005, Bull. 585, 14pp.

[2] Enkin, R.J, Baker, J., Nourgaliev, D., Iassonov and Hamilton, T.S. *Magnetic hysteresis parameters and Day-plot analysis to characterize diagenetic alteration in gas hydrate-bearing sediments*. J. Geophys. Res, 2007, 112, doi: 10.1029/ 2006JB004638.

[3] Brent, T.A., Riedel, M., Caddel, M., Clement, M., Collett, T.S. and Dallimore, S.R. *Initial geophysical and geological assessment of an industry 3-D seismic survey covering the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well; in Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada, (ed) S.R. Dallimore and T.S. Collett;* Geological Survey of Canada, 2005, Bulletin 585.

[4] Novosel, I., Spence, G.D. and Hyndman, R.D. *Reduced magnetization produced by increased methane flux at a gas hydrate vent*. Mar. Geol., 2005, 216, 265-274.

[5] Housen, B.A. and Musgrave, R.J. *Rock magnetic signature of gas hydrates in accretionary prism sediments.* Earth Planet. Sci. Lett.,1996,139,509-519.

[6] Roberts, A.P. *Magnetic properties of sedimentary greigite (Fe_3S_4).* Earth Planet. Sci. Lett., 1995, 134, 227-236.

[7] Esteban, L., Hamilton, T.S., Enkin, R.J., Lowe, C. and Novosel, I. *Gas hydrates and magnetism: Surveying and diagenetic analysis.* Geophysical Developments from SEG series, Gas Hydrates, paper accepted 2008.

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