**Biogeosciences
Discussions**

Interactive comment on "Geophysical and geochemical signatures of Gulf of Mexico seafloor brines" *by* S. B. Joye et al.

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Received and published: 20 June 2005

Disscussion and Comments.

Joye, I.R. MacDonald, J.P. Montoya, and M. Peccini 2005. Geophysical and geochemical signatures of Gulf of Mexico seafloor brines. Biogeosciences-Discussions 2,637-671.

General Comments

Over the past decade biological oceanographers have become increasingly aware that the ecology of deep continental margins is influenced by local geological and geochemical processes as well as the large-scale gradients associated with depth (Carney 2005). Focused discharge of fluids at the sediment surface is a category of such biologically important local variation. Among discharges, seafloor brines are of special

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interest due to the extreme habitat afforded to halophilic + barophilic + thermophilic + anaerobic + thiotrophic + etc. microbes. Additionally, the elemental composition of brines serve as unambiguous tracers of origins and routes. Joye and her associates make an important contribution to the growing knowledge of deep brine geochemisy and ecology. The paper certainly meets the criteria of Biogeosciences Discussion in terms of content, relevance, quality of work, and presentation.

Scientific Points

If anything, the authors are overly conservative in discussing their observations. In the following paragraphs alternate interpretations and broader contexts are presented that the authors may choose to address. Much of this discussion centers around alternate models for the origin of seafloor brines in pools closely associated with salt structures. Discussions with Dr. Jaye Cable at Louisiana State University and Dr. Paul Aharon at the University of Alabama greatly improved the interpretations that I offer. In the concluding paragraph I challenge the conclusion that the GB425 pool is less stratified and stable than the pool at GC233. The conclusion may be correct, but there are conflicts in data that call in to question the logic presented. The authors need to address the data problems identified.

While the authors choose to accentuate the differences of the two brine pools, greater consideration of similarities is indicated by the data summary for other studies (Table 2) and the various gradients illustrated. Structurally, deep Gulf of Mexico brines range from very large and conspicuous filled basins such as Orca, down to small patches of brine-charged sediments with little surface indication of ponding or flow. In between, is a wide range of expulsive pools, over-surface flows, and dammed pools. The simplest and useful null model for the main composition of these brines is seawater contact with halite followed by mixing (Aharon et al 1992). The salinity and molar Na:Cl ratio of Orca Basin (258 ppt, 0.9528) suggest minimal dilution (˜ 1:0.33 halite-contact brine : seawater) of a brine formed by direct contact with halite. By comparison, GB425 (130 ppt, 0.8467) shows a much greater 1:6 dilution, and GC233 (121 ppt, 0.8370) an 1:8

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dilution. These conclusions assume saturated salt dome brine in the range of 250-300ppt (Lerche and Petersen 1995) and a Na:Cl value of approximately 1 (Aharon et al 1992, Fu and Aharon 1998). Bottom water salinity and Na:Cl are given by the authors as 34 ppt and 0.8191. These large dilutions and other constituent concentrations inconsistent with the simple model as noted by the authors, suggest that the "soups" filling the bowls has passed through many kitchens.

With respect to salinity, Na:Cl, depleted sulfate and enriched calcium, the brine of both pools resemble the type III pore fluids of Fu (1998) and Fu and Aharon (1998). Those authors interpreted the brines as being distally derived from dissolving halite, but elevated Ca, Sr, and Ba was attributed to incorporation of Mesozoic formation waters. Their argument was strengthen with 226Ra and δ18O data. Joye et al. put forward a similar argument for locally distinct sources (i.e. fossil waters) based on Mg. It would seem that against an overall pattern of salt dissolution, there is considerable local chemical variation associated with subsurface geochemistry and circulation. The biological consequences of this, if any, are unknown.

While the authors favor fossil water as the primary brine source, it is interesting to speculate on the consequences of the simple halite contact with mixing explanation. The composition of both pools indicates that the considerable mixture of halite-contact brine and seawater takes place within the sediment column below the depth at which the pools are filled. An obvious question is the sources and forces of the admixing seawater. The most apparent sources are interstitial seawater expelled by compression or seawater drawn distally into the bottom by Rayleigh-Bernard convection associated with the relatively hot salt structure (Bennett and Hanor 1985). Of these two hypothetical mechanisms, an influx of seawater would be of considerable biogeological consequence. Sulfate would be drawn into sediments and consumed by microbial reduction deeper and at rates greater than simple diffusion or bioventilation can support.

The sulfate composition of the brines is especially important for biological effects, supporting anoxic bacterial sulfate reduction. In general (Joye et al. Table 2), brine sul-

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fates range from $<$ 1mM to approximately 3x increase relative to seawater. In the Gulf of Mexico systems, sulfate depletion is evident in the two small pools reported, but a 2x enrichment is found in the much larger Orca Basin further downslope. This same sulfate dichotomy has been noted for interstitial brines near the sediment/water interface; strongly sulfate-depleted fluids (Fu 1998) as well as fluids enriched 1.4 - 1.5x (Aharon et al. 1992). With so few samples, it is highly speculative to identify spatial trends, but sulfate depleted brines are found on the upper slope above 1000m and sulfate-enriched brines on the lower slope below 2000m. If real, this may reflect the down-slope transition from vertical diapir formation to lateral sheet flow noted by many experts (Bryant et al 1991 and references therein).

Some greater consideration should be given to geobiological explanations for why Gulf of Mexico brines vary so greatly in sulfate content. As a non-conservative constituent, sulfate concentration must represent an equilibrium between loss by microbial conversion to sulfide and addition from salt-associated anhydrite and gypsum. Microbial loss, in turn, is controlled by availability of refractory hydrocarbons and brine toxicity. It is fun to speculate that sulfate depletion in brines flowing up to the seafloor is due to sub-surface microbial reduction rather than processes in the pool itself. Subsequent loss of the resulting sulfide may be through additional microbial reduction to elemental sulfur or microbial as well as abiotic formation of metal sulfides.

Underscoring the considerable methodological challenges of the reported work are apparent inconsistencies between thermal gradients assessed by CTD and chemical gradients measured from water samples. In the GC233 pool, CTD temperatures show a fully-mixed homogenous layer from the interface to a depth of approximately 1m followed by a deeper thermocline (Fig 6A). Chemical concentrations over this same interval (Fig. 7A,B, and 8A), however, show a strong gradient underlain by a homogenous layer. The temporal sequence of these measurements is not clear from the text. Given the importance of the gradients in drawing conclusions about relative stability, the authors should address this apparent conflict, considering uncertainties in the depth axis

or temporal variation in gradient depths.

The authors propose mechanisms for methane saturation in the brine and elevated levels of ammonia that warrant additional attention. It is proposed that the brine becomes supersaturated with methane due to percolating gas bubbles, and that sediment-sorbed ammonia is washed off by the circulating high salinity fluid. The concentration of both chemicals may be due to salt effects in close proximity to the salt body. Dissolved interstitial methane should outgas along the diapir flanks due to decreased solubility in warming and increasingly saltier fluid. As subsurface mixing cools and dilutes the fluid, methane gas will redissolve and be carried upward in solution if gas and liquid share a common migration path. The existence of persistent pools and volcanoes indicates such common paths.

Of the several gradients shown, that of silica (Fig. 9) is especially interesting in the curves are modal, have similar concentration maxima, and the maxima coincide with the top of the deeper homogenous layer in each pool. Of possible explanations, it seems most likely that both pools function as particle traps with siliceous particles aggregating at a density interface. The extent to which brine pools act as death traps for larger fauna has already been noted (Macdonald 1992), and interpretation of biologically active compounds should always consider this as a possible factor.

It is repeatedly claimed that the two pools represent very different rates of fluid seepage. Indeed, this conclusion is consistent with some of the data presented and the additional discussion of dilution proved herein. It should be noted, however, that neither liquid nor gas seepage has actually be measured either in this paper or MacDonald et al. (2000). The related conclusion that GC-233 is well stratified and GB-425 well mixed, however, does not necessarily follow from inferred rates and is not supported by the data presented. Especially worrisome are the temperature plots for GB425 (Fig. 6B). Compared to the originally published figure (MacDonald et al. 2000 Figure 3), the profile taken in 1998 has been truncated and rescaled from three to one meter and translated ˜50cm downward,. The authors must explain these alterations. The original

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full three meter plot is very difficult to interpret, and if taken in conjunction with brine trapper samples (Fig. & D &C) represents a density inversion. The authors must be more specific about when the presented profiles were taken; what is the temporal relationship between CTD casts and brine-trapper data?. Ignoring these serious data problems and looking only at the presented data, the conclusion concerning stability is still ill supported. When equal depth scales are applied to the thermal profiles (Figure 6), the structure is quite similar between pools except for absolute temperature and the low 19917 values in GB425. The chemical gradients (Fig 7 and Figure 9) show both pools to be well stratified. The cline between upper and lower strata spans a greater depth at GC233, consistent with longer residence time, slower flow, and/or slower upper mixing.

Technical Corrections

The methods section includes techniques for determination of DIC, and DIC results are discussed.. The DIC data should be included.

Methods for determination of percent suspended solids need to be added.

P. 648 line 22 - fluid discharge should read gas discharge

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