THE TAHITI BARRIER REEF: A RESERVOIR FOR INORGANIC AND ORGANIC NUTRIENTS

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ABSTRACT

Interstitial water samples, from a borehole drilled in 1992 to 150m inside the north barrier reef of Tahiti, have been analysed monthly for: temperature, salinity, dissolved inorganic nutrients (PO_4, SiO_4, DIN, DIC), O_2, pH and alkalinity. Other parameters such as dissolved organics (DON, DOC) were also measured in 1994 in two sets of samples. These data show:
1- significant differences with the adjacent ocean, including a lower density for any given depth, leading to an inevitable upward movement of interstitial water
2- decrease of pH, alkalinity, DIN and DIC with depth, from the reef crest down to the carbonate - basalt interface at 116m
3- strong positive gradients of DON and DOC inside the basaltic foundation (116-150m), which then constitutes a large organic reservoir.
These results suggest that the organics coming from the basalt foundation (first end-member) are, during their circulation through the carbonates, transformed into inorganic nutrients, with consumption of dissolved oxygen. A second end-member is the oceanic surface water injected by waves forcing through the top part of the reef: the mixing of the interstitial water with this nutrients-depleted, oxygen -saturated water tends to prevent anoxia and to lower nutrients concentration. The specific properties found in the basalt interstitial waters - low alkalinity, high silicate and high DON-DOC content - are convergent with data obtained in other basaltic crusts where thermally driven-hydrothermal circulation is a general rule.

INTRODUCTION

Long series of sampling of interstitial waters in the barrier reefs of Tikehau atoll (Tuamotu Archipelago) and Tahiti high island, have shown that these interstitial waters are partly originating from deep oceanic water infiltration, either through the underlying volcanics or the carbonate framework, and are upwelled towards the top of the reef by convective transport (Rougerie and Wauthy 1993; Andrié et al 1993). A second input is made up by the turbulent injection of Tropical Surface Water (TSW) by wave surge at shallow depth on the reef crests and outer flanks, permanently exposed to oceanic high energies. As the six boreholes already drilled in Polynesian reefs did not exceed 50m, a deeper borehole down to 150m was drilled in October 1992 on the Tahiti north barrier reef, in order to sample deeper levels and to reach the limestone- basalt interface. The main aim of this program was to characterize the origins, transformations and pathways of the interstitial waters thought to circulate in the basaltic foundation, then endo-upwell and interact with the carbonate matrix of the reef structure.

MATERIALS AND METHODS

The borehole (referenced as P7) is located on the Tahiti reef barrier, in the north of the Papeete harbour. The description of the sampling procedure at 12 levels (5, 10, 20, 30, 50, 60, 80, 100, 115, 130, 140, 150 m) is reported in Fichez et al. (1995). The waters, pumped with peristaltic pumps from polyamide tubes inserted in the hole, were rapidly analysed in the ORSTOM lab at Tahiti: dissolved oxygen, with a precision of 0.05 ml/l; pH, with a precision of 0.01 unit; total alkalinity (with the potentiometric titration method) with a precision of 0.01 meq/Kg; redox potential, with a precision of 5 mV; salinity, with a precision of 0.002 psu. Inorganic nutrients analysis were performed by the classical spectro-colorimetric method on unfiltered water samples, with a precision (in μM) of 0.05 for PO_4-P, 0.1 for NO_2-N, NO_3-N, NH_4-N and 0.2 for SiO_4-Si. Dissolved organic nitrogen (DON) has been computed, with a precision of 0.2 μM, from total nitrogen obtained by U.V. oxidation of samples after substracting the amount of dissolved inorganic nitrogen (DIN), alleged to be the sum of NO_3 + NO_2 + NH_4. Dissolved organic carbon (DOC) was analysed according to the high-temperature catalytic oxidation technique (Cauwet 1994), with a precision of 0.1 mM; dissolved inorganic carbon (DIC) was computed from pH and alkalinity values, with a precision of 0.02 mM.

INORGANIC AND ORGANIC COMPONENTS

The drilled core has revealed that the structure of the borehole P7 is made up, from the reef top to 116m, by permeable carbonates with a porosity between 30 and 50%. From 116m to 150m, the structure is basaltic, with heterogeneities and fissures. Salinity and tracer data (Fichez et al 1995) have allowed to differentiate several water masses: inside basalt, a Basaltic Interstitial Water (BIW) underlying a Reef Interstitial Water (RIW) in the 100-0m range; Oceanic surrounding waters are TSW in the 0-150m layer, and Antarctic Intermediate Water (AIW) beyond 500m depth (Rougerie and Rancher 1994).

Inorganic nutrients, pH and alkalinity.

Interstitial dissolved phosphates are in the range 0.5 to 1.5 μM, with a positive gradient from the top to the bottom of the hole; TSW has only 0.2 μM in PO_4. Silicate content is between 80 and 280 μM, which represents an enormous enrichment compared with the 1 μM in TSW. Nitrogen forms have peculiar vertical profiles: NH_4 is abundant in RIW but, as NO_2 and NO_3, tends to wane in BIW. However, these interstitial values are at least one order of magnitude higher than in the oligotrophic TSW. Being saturated in oxygen (around 5 ml/l), that oceanic water can bring down oxygen from the top part of the reef matrix in which it is consumed by oxidation / mineralization processes.
The buffering effect due to the high ionic product of the ocean is expressed by the great stability of pH and total alkalinity found in the TSW, where these parameters are respectively 8.30 ±0.03 and 2.46 ±0.04 meq/kg. In the interstitial system, the recorded values are very different: pH is between 7.70 and 7.72 in the first 80 meters and decreases to 7.55 at the bottom hole. That last value is lower that the pH of the deep ocean (7.90), that means important biochemical reactions, involving total consumption of O_2 and release of CO_2 and reduced forms, to happen inside the basaltic part. Total alkalinity in the top layer of the RIW is similar to that of the oceanic TSW, but decreases regularly with depth to reach 1.40 meq/kg at 150m, with a steep gradient between 60 and 100m. These very low values mean a loss of almost half the basidity excess, when compared with the oceanic sea water, whose minimum alkalinity is around 2.2 meq/l.

Distribution of C and N forms.

The vertical distribution of the main forms of carbon (dissolved inorganic carbon DIC; dissolved organic carbon DOC) and nitrogen (dissolved inorganic nitrogen DIN; dissolved organic nitrogen DON) tends to confirm the specificity of the interstitial system (Figure 1). The mean vertical profile of DIC shows a strong decrease through the carbonate pile, with values of 2.2 mM in the reef upper part to 1.4 mM in the basalt (Figure 1a). That trend mirrors the vertical profiles observed for pH and alkalinity, and confirms that the BIW is out of equilibrium with its basaltic environment: any decrease in pH should be logically associated with an increase in DIC, due to a release of CO_2 governed by the process of oxidation / mineralization of detritic / organic material. This is apparently not the case in the basaltic system. These paradoxical properties of the BIW (low alkalinity -pH and low DIC) can however be understood when the DOC distribution is taken into account: DOC values are low in the carbonate reef (around 2mM) but rapidly rise down from the basalt interface to reach more than 15 mM at 150m. The strong anti correlation between the vertical profiles of DIC and DOC implies the existence of a close linkage in their evolution with depth; that can reflect an oxidation / mineralization of DOC, a process able to stoichiometrically lowers DOC and rises DIC. This hypothesis is sustained by the distribution of the two main forms of dissolved nitrogen, DIN and DON : Figure 1b shows a same opposite evolution with depth, with high DON - low DIN in basalt and the opposite pattern in the limestone. It is known that the biochemical processes of organic matter oxidation are slower for nitrogen forms than for phosphorus, and will produce at first NO, NH_4, NO_2 and NO_3; that sequence fits well with the dominance of NH_4 (rather than NO_3) found at the level of the basalt-limestone interface. For both C and N forms, the steeper gradients appear between 100 and 60 meters, in the core of the RIW, where the mixing rates between the two end-members TSW and BIW are probably optimal. Such mixings can then strongly contribute to the rapid shift observed in the organic - inorganic balance of the interstitial system.
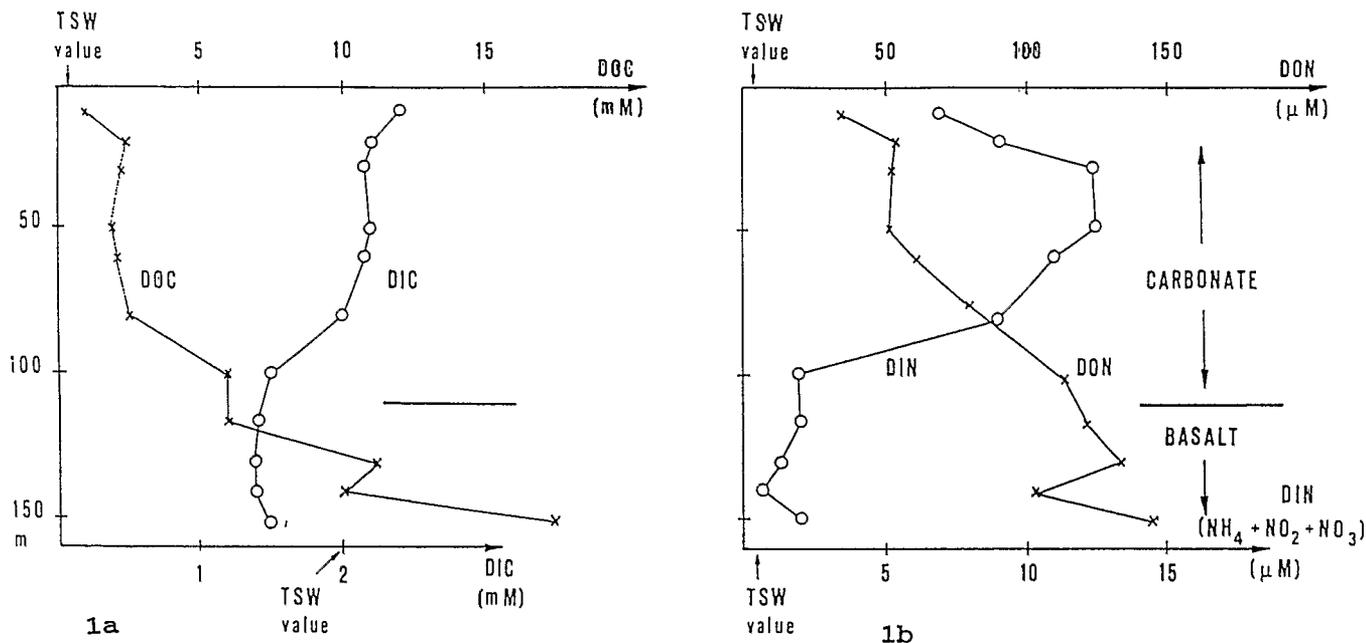
Fig. 1: (a) Vertical profiles of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC); (b) Dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN). The basalt high organic load decreases when the BIW pervades the carbonate; the inorganic nutrients follow an opposite shift, that suggests a close linkage between these two members.

ORIGINS OF THE ORGANIC RESERVOIR IN THE BASALT.

To explain the high amounts of organic matter found in the BIW we can at first consider the potential impact of any sea water direct penetration inside the basalt. Oceanic waters, either TSW or deeper masses (Antarctic and Deep Waters) have a low dissolved organic load (Tanoue 1993), one to two orders of magnitude less than was measured in the BIW. Different processes, like leaching of the detritic flanks covering the deep part of the island by intruding waters, or direct injection of organic matter from the living veneer of the reef, can constitute positive inputs: they are certainly insufficient to explain both the high values in DOC and DON, and the positive gradients (with increasing depths) found in P7. That leads to consider the possibility to have a permanent organic reservoir, either in particular and / or in dissolved form, trapped inside the basalt, perhaps since its cooling after the peak of volcanic activity having created the island of Tahiti 1 million years ago. Data gained at hydrothermal vents located on basaltic ridges can show high contents of CH_4, CO_2, CO, NH_4 etc.(Von Damm et al.1985), revealing the presence of an interstitial reservoir of organic matter. The way in which that organic matter has first been accumulated, then degraded and dissolved in these thermally-driven pore waters, is certainly a complex pathway, tightly constrained by physico-chemical parameters (hydraulic conductivity and age of the basaltic crust, heat flux, flow rates, acidity and redox potential, etc.). But as stressed by Wheat and McDuff (1994), the degradation of deep organic matter is greater in hydrothermal systems than in non-hydrothermal settings. And so, depending the regional conditions, the thermo-convective internal circulation may introduce back to the ocean old dissolved organic molecules previously sequestered. These carbons species are systematically C-13 depleted, and the same shift has already be noted in the pore water of our P6 borehole, located 800m away from P7 (Andrié et al. 1993).

INTERSTITIAL CIRCULATION AND MIXING

Sea water circulation in basalt, generally by thermo-convective process is now a well-established fact (Mottl and Wheat 1994) that concerns even the ridge flanks where heat flux can be significantly lower than in the active ridge axis. These internal circulation and upwelling have important consequences, both inside the basalt (rock-water interaction leading to ionic exchanges) and in the zones of seepages where precipitations, biocementations and biomineralizations can occur (Charlou et al .1991). Albeit the range of ionic modifications undergone inside basalts by the intruding deep sea water is very large, some common shifts are generally observed: the thermo -convective / hydrothermal waters are enriched in Mn, Fe, Si and their alkalinity can considerably differs from oceanic values. In some hydrothermal vents (in the

range from high to cold temperature) alkalinity can outpass 100 meq/Kg (Simoneit 1990); in others systems, alkalinity can be very low, or get negative values. The alkalinities measured in the pore water of P7 borehole show a brutal decrease in the basalt layer (115-150 m.), with a mean value of 1.4 meq/Kg in BIW: That represents a loss of almost half of the basidity-excess measured both in TSW and in AIW. As alkalinity is a parameter which sums any kind of dissolution / precipitation processes, its degree of anomaly is indicative of its degree of desequilibrium, when compared with a normal sea water. The low alkalinity found in our BIW tells at least that, after its penetration in the basalt, the deep oceanic water has undergone important ionic exchanges and precipitations, themselves controlled by the dynamic of the interstitial circulation. That upwards circulation and mixing can explain the strong gradients observed in pH and alkalinity above the basalt / limestone interface: the BIW, being unsaturated in carbonate-aragonite, is potentially very aggressive to any carbonate structure and will tend to dissolve the weakest and less cemented parts of the reef. The RIW is then progressevely enriched in carbonate by *in situ* dissolutions and by mixing, both processes which must inevitably increase pH and alkalinity and counterbalance acidification due to mineralization.

CONCLUSION

A first implication deals with the transformations and diageneses that the BIW can trigger when it upwells in the reef matrix: the original permeability of that limestone exceeds 10 Darcy and the thermo-convective flotability of the fluid (Rayleigh number) is more than 10 times the critical value, that guarantees an easy move for the interstitial water (Ormond et al. 1995). But being unsaturated in aragonite-carbonate, the flow of BIW is not in ionic equilibrium with the basement of the reef and tends to react with it: that feed-back between the fluid and the matrix is propicious to karstifications / dissolutions processes driven by the velocity of the fluid and the chemistry of the system. This interactivity enhances the porosity / permeability of the matrix and avoids its clogging, even on a large time frame. The informations given by the vertical distribution of inorganic and organic components allow to precise the mixing rates of the two end-members waters penetrating the carbonate, BIW (from the reef basaltic foundation) and TSW (from the reef upper part). The BIW constitutes an important reservoir of dissolved organic matter (100 to 1000 times the oceanic values) that implies complex and badlly known accumulations processes and microbial activity. When, entrained by the interstitial circulation it reaches the carbonate pile, that organic load is rapidly diluted (by the TSW component) and oxidated, that liberates an equivalent amount of inorganic nutrients. A second source of organic and detritic matter (both in dissolved and particular form), is probably originating from the coral-reef ecosystem, from which it is introduced inside the reef

matrix by turbulences and wave action; a certain proportion of the organic production of the reef is then internally stored and recycled, that liberates regenerated nutrients and consumes oxygen (Rougerie 1996). When anoxy is reached, the interstitial organic pool, however its precise origin, can be stored and slightly submit to different maturation steps; the resulting products could be linked with the hydrocarbon signatures already detected in atolls and P6 boreholes (Bouloubassi et al. 1992): these biomarkers are derived from bacterially induced alteration products, in conjonction with *in situ* thermo-maturation process. We can then question their significance in term of carbonate diagenesis and reef growth. Some analogies can exist with other coral reef provinces as in the Gulf of Mexico where Roberts (1992) has showed that carbonate buildups are highly correlated with hydrocarbon seeps. The specific consequences of an internal circulation of organic-rich fluids on carbonate reefs development has been stressed by Hovland (1990). It is there of a growing acceptance that pore waters, moved by density-driven or hydrothermal head, can trigger in their zone of seepage a very specific response, in term of mineral precipitation, bio-cementation and bio-development.

Our P7 data set point out that an active circulation of BIW, from the basalt down to the limestone pile, can justify the anomalous and specific distributions observed in alkalinity, salinity, nutrients and organic matter contents inside the reef. Permanently recharged in its deep layer by the carbonate-unsaturated BIW, and in its upper layer by the carbonate-supersaturated TSW, the RIW constitutes a fluid in permanent ionic reajustement all along its pathway. The core of this barrier reef can then be viewed like a bio-reactor efficiently transforming the organic load, mainly coming from the basaltic reservoir, into inorganic nutrients which are entrained by the interstitial circulation and whose role in the reef metabolism continue to be an open question (Tribble et al. 1994).

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REFERENCES

Andrié C, Bouloubassi I, Cornu H, Fichez R, Pierre C, Rougerie F (1993) Chemical and tracer studies in coral reef interstitial waters : Implications for endo-upwelling circulation. In : Proc. 7th Int Coral Reef Symp. Guam 2: 1165-1173

Bouloubassi I, Saliot A, Rougerie F, Trichet J (1992) Hydrocarbon geochemistry in coral reef pore waters. Vol. 1, Water-Rock Interaction, Kharaka and Maest (Editors), Rotterdam : 271-274

Charlou JL, Bougault H, Appriou P, Jean-Baptiste P, Etoubleau J, Birolleau A (1991) Water column anomalies associated with hydrothermal activity between 11°40' and 13° N on the East Pacific Rise. Deep Sea Research 38 (5): 569-596

Cauwet G (1994) HTCO method for dissolved organic carbon analysis in seawater: influence of catalyst on blank estimation. Mar. Chem. 47:55-64

Fichez R, Rougerie F, Déjardin P, Harris P (1995) Stucture géologique et étude des eaux interstitielles du récif barrière de Tahiti. Rapport final Conv. N° 378, ORSTOM-Group. Port Autonome/Compagnies Pétrolières. Tahiti: 44 p

Hovland M (1990) Do carbonate reefs form due to fluid seepage ? Terra Nova, 2 (1): 8-18

Mottl MJ and Wheat CG (1994) Hydrothermal circulation through mid-ocean ridge flanks: fluxes of heat and magnesium. Geochim. et Cosmochim. Acta. 58-10: 2225-2237

Ormond A, Ortoleva P, Rougerie F (1995) Self-organisation in the evolution of the carbonate matrix of the coral reefs. Int. Workshop on Reefs and Carbonate Platforms, Sydney, Abstr.

Pierre C, Vergnaud-Grazzini C, Faugeres JC (1991) Oxygen and carbon stable isotope tracers of the water masses in the Central Brazil Basin. Deep-Sea Res 38: 597-606

Roberts HH (1992) Reefs, Bioherms and Lithoherms of the Northern Gulf of Mexico: the important role of hydrocarbons seeps. Proc of the 7th Int Coral Reef Symposium, Guam 2: 1121-1128

Rougerie F (1996) In situ processes in reef interstitial waters: implication for reef growth / calcification. Bulletin de l'Institut océanographique, Monaco, n° spécial 14 (4): 47-59

Rougerie F and Wauthy B (1993) The endo-upwelling concept: from geothermal convection to reef construction. Coral Reefs 12: 19-30.

Rougerie F and Rancher J (1994) The Polynesian South Ocean: Features and circulation. Marine Pollution Bulletin 29 (1-3): 14-25

Simoneit BRT (1990) Petroleum generation, an easy and widespread process in hydrothermal systems: an overview. Applied Geochemistry 5: 3-15

Tanoue E (1993) Three vertical profiles of dissolved organic carbon in the North Pacific. Mar. Chem. 41: 261-264

Tribble GW, Atkinson MJ, Sansone FJ, Smith SV (1994) Reef metabolism and endo-upwelling in perspective. Coral Reefs 13 (4): 199-201

Von Damm KL, Edmond JM, Grant B, Measures CI, Walden B, Weiss RF (1985) Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. Geochim et Cosmochim Acta 49: 2197-2220

Wheat CG and McDuff RE (1994) Hydrothermal flow through the Mariana Mounds: Dissolution of amorphous silica and degradation of organic matter on a mid-ocean ridge flank. Geochim et Cosmochim Acta 58 (11): 2461-2475.