Revista Latino Americana de Geoquimica Organica, Vol. 5, pp. 39-46, 1999

USE OF QUARTZ CEMENTATION KINETIC MODELING TO CONSTRAIN BURIAL HISTORIES. EXAMPLES FROM THE MARACAIBO BASIN, VENEZUELA

Perez, R.J.[1], Chatellier, J.I.[2] & Lander, R.[3]

[1] PDVSA-Intevep, Los Teques, Venezuela.
Presently at University of California, Santa Barbara, Geological Sciences Department, Web Hall Bldg. 526, CA-93106, USA.
[2] PDVSA-Intevep, Departamento de Ciencias de la Tierra, Apdo. 76343 Caracas 1070A, Venezuela.
[3] GEOLOGICA, PO Box 8034 4003, Stavanger, Norway.

ABSTRACT – The paper presents a kinetic expression for quartz precipitation that is consistent with field observations in areas of the Maracaibo basin where burial histories are well constrained. The quartz precipitation kinetic expression was then used in concert with a numerical modeling code (EXEMPLAR^{tm}) as an independent means of estimating paleotemperatures. The model was applied to certain areas of the Maracaibo basin where several tectonic events have complicated paleothermal reconstructions and where vitrinite reflectance trends as well as other maturity thermal indicator are uncertain. Numerical simulations of quartz cement precipitation in quartoze sandstones of the Misoa Formation in the Maracaibo Basin validated the well known burial reconstruction (previously calibrated using vitrinite reflectance data) and helped reconstruct thermal histories where vitrinite reflectance trends were uncertain. The application of sandstone diagenetic numerical tools, used together with organic maturity parameters, can contribute strongly to understanding the overall history of thermally complicated areas.

RESUMEN – Se presenta una expresión cinética para la precipitación de cemento de quarzo, consistente con observaciones de campo en la Cuenca del Lago de Maracaibo, en donde las historias de soterramiento son bien calibradas. La expresión cinética de precipitación de cemento de cuarzo fue usada en conjunto con un simulador numérico (EXEMPLAR^{tm}) como paleotermómetro independiente para entender la historia termal del area.
El modelo fue aplicado a varios campos petroleros, en donde múltiples eventos han dificultado la reconstrucción paleotermal y en donde los valores de reflectancia de vitrinita, asi como otros indicadores de madurez termal, son inciertos. La simulación numérica de la cementación de cuarzo en areniscas de la Formacion Misoa, validó modelos de soterramiento previamente calibrados con reflectancia de vitrinita, y colaboró con la reconstrucción termal en ausencia de reflectancia de vitrinita. La aplicación de herramientas numéricas diagenéticas en conjunto con otros indicadores de madurez termal, hacen posible la reconstrucción termal de areas tectonicamente complicadas.

Keywords: *Quartz cement, Maracaibo, Diagenesis, Venezuela*

INTRODUCTION

Both vitrinite reflectance and quartz cement abundance have been shown to be useful paleothermal indicators in the past (Lander, 1997b). However, while vitrinite reflectance tends to be controlled by the maximum temperature, the rates of quartz cementation tend to be more sensitive to the elapsed time at temperatures over 70°C (Walderhaug, 1994 and 1996). Thus, if quartz cement is present, the combined constraints provided by the two thermal indicators makes possible the reconstruction of thermal histories with high precision.

Kinetic parameters, consistent with field observations and with well known burial histories, were developed for quartz cementation in a Venezuelan basin. The purpose of obtaining the kinetic expression for quartz cementation was to use it as an independent paleothermometer in different areas of the basin where vitrinite reflectance as well as other maturity parameters (such as Rock-Eval and spore color alteration) were uncertain.

The kinetic parameters were used in concert with quartz precipitation model of Lander and Walderhaug (1999). The applicability of this model in Venezuelan basins was first shown by Awwiller and Summa (1997).

The diagenetic quartz numerical modeling was applied to the Zulia Oriental Region (eastern part of Maracaibo Lake basin) western Venezuela, where multiple tectonic events (and uncertain values of different paleothermometers) make the burial reconstruction of certain areas difficult to asses.

Measuring and understanding vitrinite reflectance trends in oil fields of the Zulia Oriental Region (ZOR) has not historically been an easy task. In some specific wells, vitrinite reflectance values plotted against depth have shown no identifiable trend, due to high scattering of the data. For instance, the Onshore Bachaquero Field (Figure 1) shows substantial differences in vitrinite reflectance trends compared to the neighboring Offshore Bachaquero Field. Although a great number of these vitrinite reflectance anomalies are currently explained with relatively recent structural models of the area (Roure *et al.*,1997), complications in the interpretation still remain unclear.

The Zulia Oriental Region (ZOR) is located in the eastern part of the Maracaibo basin, western Venezuela (Figure 1). It is a complex area that has posed significant challenges for structural interpretation as well as burial and thermal modeling (Chatellier *et al.*,1998; Rodriguez *et al.*, 1997; Roure *et al.*, 1997). Within the ZOR, the quartz cementation model was focused in the Eocene Misoa Formation, specifically in its upper section, which currently constitutes the primary exploration target in the area.

ZOR - GENERAL GEOLOGY

Tectonic Setting

During the Cretaceous, the ZOR was located on an extensive passive margin which formed the northern end of the South American continent (Lugo and Mann, 1995; Parnaud *et al.*, 1995). Convergence of the Caribbean Plate during the Paleocene and Early Eocene resulted in the emplacement of the Lara Nappes and the formation of a rapidly subsiding foreland basin to the northeast of the continent (Roure *et al.*, 1997). In the ZOR and present day Lake Maracaibo areas, subsidence took place in stepwise fashion across a set of WNW-ESE trending normal faults, and also resulted in the reactivation of a preexisting set of major N-S trending faults.

In the Middle Eocene the Misoa delta system prograded in a northeast direction across Lake Maracaibo.

During the late Middle Eocene, prolonged compression culminated in widespread uplift and emergence of the central Maracaibo basin and the inversion of both the N-S and NNW-SSE trending faults (Lugo and Mann, 1995).

Evidence for late Eocene to Miocene extension has also been documented north of the

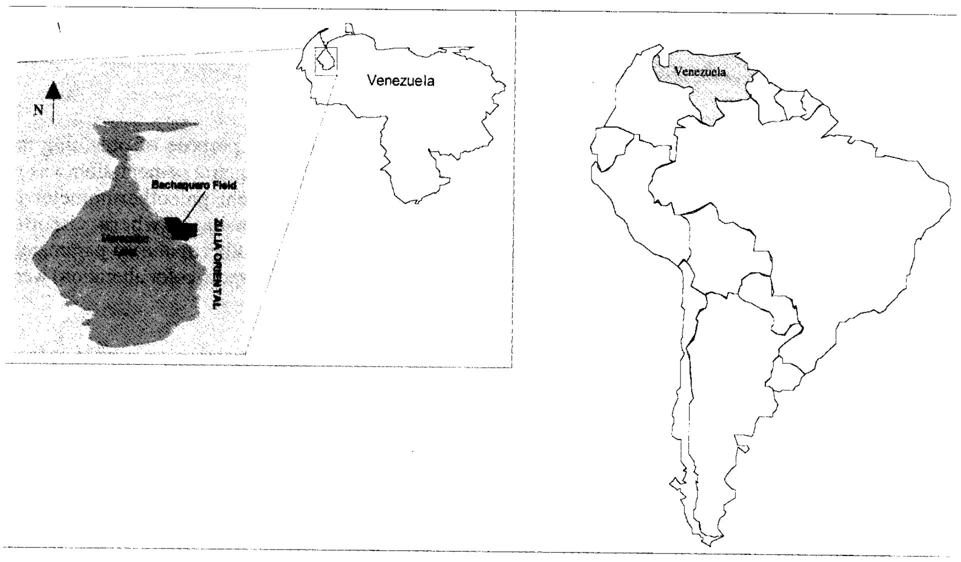

Figure 1. Location map of the Venezuela, Maracaibo Lake basin and the Zulia Oriental Region

Zulia Oriental (Roure *et al.,* 1997). In the late Miocene, NNW-SSE plate convergence resulted in the uplift and tilting of major parts of Lake Maracaibo and Zulia Oriental.

This complex polyphasic tectonic history is associated with rapid Eocene subsidence rates and different erosion thicknesses (varying between 200 and 2000 meters) depending upon the structural element present in the area (Rodriguez *et al.,* 1997).

Stratigraphy

The sedimentology of the Misoa Formation in the ZOR has been extensively studied in the past (Ghosh *et al.,* 1990; Gonzalez De J. *et al.,* 1980; Perez *et al.,* 1997; Van Venn, 1972). The Misoa Formation has been classically referred to as a deltaic to tidal influenced deltaic environment (Gonzalez De J. *et al.,* 1980) with high shallow marine sequences in the ZOR (Ghosh *et al.,* 1990; Perez, 1998).

The stratigraphy of the Misoa Formation has been informally divided from base to top in four distinctive units: the lower and upper "C" sands overlain by the lower and upper "B" sands (Ghosh *et al.,* 1990). In general, in the ZOR, from 58 to 49.5 m.y. (late Paleocene to early Eocene) during the deposition of the "C" sands, the shoreline was located within the present-day Maracaibo Lake and was aggradational to mildly progradational. This was followed by a phase of northeastward progradation across the ZOR up until 44 m.y. after which rapid subsidence resulted in a widespread transgression throughout the area from 44 to 39.5 m.y. (middle to late Eocene). A summary of the stratigraphy of the area under investigation has been summarized in Figure 2.

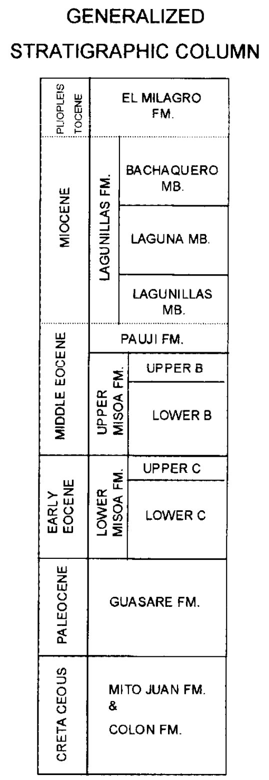

Figure2. Stratigraphy of the area under investigation. The Eocene sextion corresponds essentially to the Misoa Formation. All samples were taken from the Upper Misoa Formation. Dashed line represents unconformity. Lithological description of each formation can be found in Gonzalez de Juana et al. (1980)

All of the samples studied were taken from the Misoa Fm. and particulary from the Upper B sands, between 41.5 m.y. and 44 m.y.

PETROGRAPHY

Conventional petrography using a standard transmitted light microscope was performed on 21 different samples from 5 different wells, in order to determine microscopic textures and mineral composition. The modal composition of the sandstones was determined with the petrographic microscope by point count (500 point counts per thin section). The results from the point count were corrected using the relative percentage of quartz cement obtained through cathodoluminescence (CL) image analysis. Seven samples were chosen as the bases for the numerical modeling. The samples were chosen based on the high relative abundance of quartz cement and low relative abundance of clay size material, because they would fit better the theoretical model (Lander and Walderhaug,1999).

On these seven samples, a combination of backscatter electron microscopy analysis (BSE) and CL image analyses was used to quantitatively estimate the grain size, sorting and clay coating of the detrital framework.

Quartz precipitation rate is highly dependent on the total amount of surface area available for growth (Walderhaug, 1994 and 1996). The total surface area is in turn, highly dependent on grain size, sorting, and the extent of coating (Bethke, 1996; Oelkers, 1996)

QUARTZ CEMENTATION MODELLING

EXEMPLAR^{tm} (Lander and Walderhaug, 1999) was the numerical simulation code used to model quartz cementation and sandstone compaction. EXEMPLAR^{tm} is a diagenetic numerical simulator based on empirically calibrated models of compaction and quartz cementation.

Model Assumptions

Quartz cementation simulation in EXEMPLAR^{tm} assumes that the cement is derived from nearby stylolites, and that the three controlling steps of quartz cementation are 1) silica dissolution 2) diffusion / advection and 3) precipitation, being silica precipitation the rate limiting factor (Lander and Walderhaug, 1999). The fundamental parameters of the quartz cementation modeling are the kinetics of silica precipitation and the available surface area for quartz cement overgrowth in optical continuity. The kinetics of precipitation per unit of surface is a function of temperature and is defined by

$$Rate = a\ 10^{(bT)}$$

Where "*a*" is the preexponential parameter (in mol/cm^2 s), "*b*" is the exponential constant in degrees C^{-1}, and "*T*" is the temperature in ^{0}C (Walderhaug, 1994). Using the appropriate conversions the *Rate* expression can be converted into an equivalent Arrhenius formula.

According to Lander and Walderhaug (1999), because the numerical simulator assumes small linear increments in temperature, *T* can be expressed by linear functions of time, and *Rate* can be written as a function of the form:

$$qcv = \frac{m}{d} Aa \int_{0}^{timestep} (10^{b\,[Cn \times tstep + dn]})\, dt$$

Where "*qcv*" is the volume of quartz (in cc) that precipitates during one time step "*n*", "*m*" is the molar weight of quartz (60.08 g/mol), "*d*" is the density of quartz (2.65 g/cc), "*A*" is the quartz surface area (cm^2), "*tstep*" is the duration of the timestep (m.y.) converted to seconds, "*Cn*" is the heating rate (C/s) for each time step and "*dn*" is the initial temperature for each time step "*n*".

INPUT PARAMETERS

The model requires time temperature data as basic input, which is obtained through burial/thermal histories. The model also requires, as basic input, initial porosity, sandstone composition and textural parameters (as detrital grain size) in order to determine the total reactive surface area.

Burial and Thermal History

Burial histories were generated using BasinMod^{tm} (Platte River, 1995) and were heavily based on Rodriguez *et al.,* (1997) thermal model.

Rodriguez et al. (1997) model assumes an increase in the heat flux from 52 mW/m^2 to 58 mW/m^2 during the Lower Eocene (59 to 49 m.y.) due to the extensional phase caused by the tectonic charge of the Lara Nappes into the northern part of Zulia Oriental, and an exponential decay in the heat flux from 58 mW/m^2 to 50 mW/m^2 (values obtained from bottom hole temperatures) since the Upper Eocene until today.

The range of thermal conductivities was reduced compared to those of Rodriguez et al. (1997). We assumed thermal conductivities between 0.0092 and 0.008 cal/cm sec for sandstones and between 0.0065 to 0.00387 cal/cm sec for sandy shales and shales respectively based on calibration of previous models in other regions of the Maracaibo Basin. This change decreased the temperatures by approximately 10°C, showing a better calibration with vitrinite reflectance.

The amount of erosion linked to the post-Eocene unconformity was estimated from Ro profiles and sonic logs using the methodology of Perez *et al.,* (1997). These estimations fluctuate between 150 m and 1900 m approximately, depending upon the structural characteristic of the penetrated strata (Roure *et al.,* 1997).

Sandstone Composition and Texture

The sample set used to obtain the best fit of the quartz cementation kinetic parameters were quartz arenites containing less than 5% of clay minerals and also less than 5% between potassium feldspar and/or lithic fragments. We chose clean samples because it is thought that they would fit better the theoretical model (Lander and Walderhaug, 1999).

Grain size was measured using CL images because in the Misoa Formation, determination of detrital quartz grain diameters using a petrographic microscope tends to result in overestimation due to the occurrence of quartz overgrowths.

Petrographic studies of similar sandstones in the Misoa Formation indicate that about 5% of the quartz grain surfaces have clay coatings (Perez *et al.,* 1997 and Perez, 1998).

A value of 47% was chosen as initial intergranular volume (IGV), following previous studies of modern sediments (Lundegard, 1992).

QUARTZ KINETIC PARAMETERS FOR ZOR

Walderhaug (1994) calculated a range of values for the precipitation rates of quartz cement, varying from 9.8 E-21 moles/cm^2 sec to 1.9E-18 moles/cm^2 sec for sandstones in the North Sea basin.

For the quartz cementation modeling in the Zulia Oriental Region, a pre-exponential constant value of 1.98E10-22 (in mol/cm^2 s) and an exponential constant of 0.022 (in degrees C^{-1}) were found to be the best fit to field observations. Similar rates of quartz precipitation would be obtained using an Arrhenius expression with an activation energy of 1.52 kcal/mol and a frequency factor of 2.6E-11 sec^{-1}.

Comparison of the predicted and measured abundance of quartz cement is shown in Figure 3.

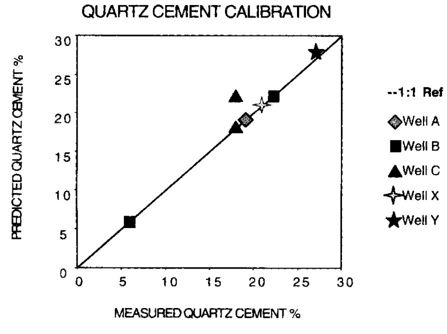

Figure 3. Correlation between observed amount of quartz cement and predicted amount of quartz cement. In each well at least one sample was used for the calibration of the model. The prediction was performed by the numerical model.

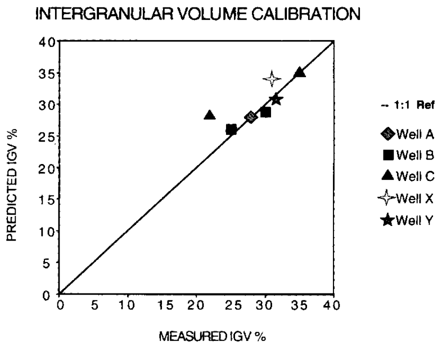

Figure 4. Correlation between measured and predicted intergranula volume (IGV). In each well at least one sample was used for the calibration of the model. The anomalous point is associated with a major unconformity and shows evidence of extensive secondary porosity which he model prediction understimates.

Using these parameters in areas of the ZOR with well constrained burial histories, all but one simulation produced excellent agreement between measured and calculated quartz cement. The anomalous point is associated with the development of secondary porosity caused by extensive potassium feldspar dissolution, due probably to unsaturated fluid flux. The high secondary porosity due to k-spar dissolution increases the relative proportion of detrital quartz and quartz overgrowth, thus making the quantification of quartz cement and intergranular volume (IGV) higher than predicted (Figure 4).

TESTING THE KINETIC MODEL IN UNKNOWN AREA OF ZOR

Once the rate of quartz precipitation was found using well known burial histories, we proceeded to use the diagenetic model and kinetic parameters and to test the thermal reconstruction of two areas of the ZOR. In these two areas, the burial history reconstruction was uncertain, due to presence of uncertain vitrinite reflectance values and lack of others maturity indicators.

Burial Histories Tests

Test in Area 1

In the area 1, the reconstructed burial history of Well "X" (Figure 5) seemed particularly questionable because it had much higher vitrinite reflectance values than nearby wells (thus, resulting in higher modeled temperatures than nearby wells). High vitrinite reflectance values could not be geologically explained. Regardless,

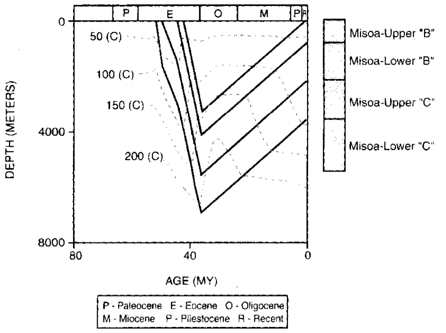

Figure 5. Burial history of well "X"

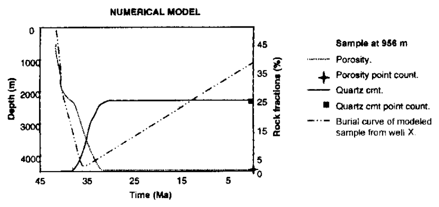

Figure 6. Results from the numerical model of quartz cementation, from Well "X" sample at 956 meters.

simulating quartz cementation with the Lander and Walderhaug (1999) model using as input the time-temperature data from the questionable thermal model resulted in agreement with cement abundances quantified under CL images (Figure 6).

Although the eroded thickness was very consistent with regional trends, sensitivity analyses were introduced by decreasing the total eroded sediment column by 10%, 15%, and higher percentages. These sensitivities resulted in proportional lower paleotemperatures.

In all the sensitivity studies, results from the quartz cementation numerical modeling significantly underestimated quartz abundance when paleotemperatures were 10°C cooler than previous values.

These results provide substantial support to the reconstructed thermal history and illustrate the sensitivity of the quartz precipitation kinetics to the time-temperature input data.

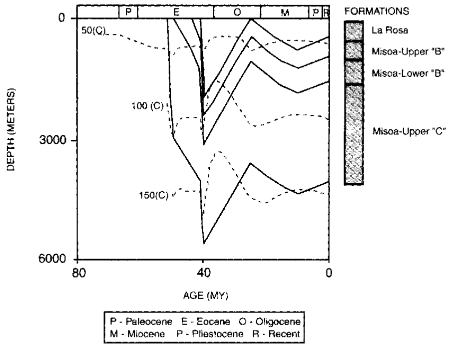

Figure 7. Burial history of Well "Y"

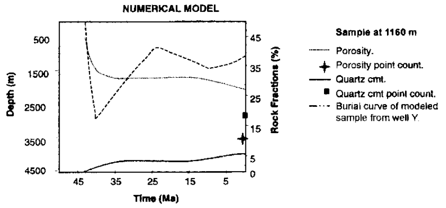

Figure 8. Results from numerical model of quartz cementation, from Well "Y" sample at 1160 meters

Test in area 2

In the area 2, the burial/thermal reconstruction for strata penetrated by well "Y"(Figure 7) resulted in vitrinite reflectance predictions that were lower than the measured values (resulting in lower modeled paleotemperatures than nearby wells). The inaccuracy of this thermal reconstruction was confirmed by the quartz cementation numerical results, which significantly underestimated CL based measurements (Figure 8).

Eventually, unsolved complications in burial histories could result in significant uncertainties that affect the consistency of thermal models proposed for the penetrated strata by wells, hence altering the timing of petroleum generation, expulsion and migration. In absence of successful thermal indicators, quantitative kinetic modeling of quartz cement, if present in the basin, could allow ascertation of paleotemperatures.

It should be noted that the quartz cement paleothermometry cannot be extended to older units (such as La Luna Formation, source rock intervals) due to the absence of samples necessary for model calibration. In the ZOR, older and deeper formations may have been obliterated by some more complex tectonic events.

CONCLUSIONS

Sandstone diagenetic properties can

provide valuable constrains on thermal history, particularly when combined with other thermal indicators.

Quartz cement precipitation rates in the Zulia Oriental Region can be predicted using the kinetic rate expression of Walderhaug (1994) with a pre-exponential constant value of 1.98E10-22 (in mol/cm^2 s) and an exponential constant of 0.022 (in degrees C^{-1}).

The quartz cementation paleothermometry provides a strong confirmation of thermal reconstruction in the ZOR that has been previously developed using vitrinite reflectance. Unlike vitrinite, quartz cementation is highly sensitive to the amount of time spent under elevated temperatures.

Measurements of vitrinite reflectance and the estimation of other important parameters such as eroded thickness, assumption of heat flow, and thermal conductivities are not exempt from subjectivity and error, but thermal complexities could be overcome by integrating quantitative diagenetic tools such as quartz cementation.

ACKNOWLEDGEMENTS

The authors wish to thank PDVS and GEOLOGICA for providing the data, funding and authorizing the publication of this paper. We would also like to thank S. Stookey for CL analyses as well as Emma Perez, Thomas Neely, and Drs. T.L.Dunn and S.K.Ghosh for stimulating discussion and critical review. And specials thank to Dr. Alicia Wilson whose critical review helped improve the style and organization of this manuscript.

REFERENCES

Awwiller D. N. & Summa L.L. 1997 Quartz cement volume constrain on burial history analysis: An example from the Eocene of Western Venezuela. American Association of Petroleum Geologists and Society of Economic Paleontologists and Mineralogists Annual Meeting, *Abstracts* **6:** 66.

Bethke Craig., Ed. 1996 *Geochemical Reaction Modeling. Concepts and applications.* Oxford University Press Inc. New York.

Chatellier, J-Y., Moreno, O., Zambrano, C., Mendez, M., Ruggiero, A., & Sarzalejo, S. 1998 Correlation between vitrinite reflectance and sequence stratigraphy, methodology and examples from the tertiary of western Venezuela. VI Latin-American Congress of Organic Geochemistry, *Abstracts* (CD.)

Ghosh, S.K., Di Croce ,J., Isea, A. & Gonzalez, C. 1990 Control of facies, burial history, and oil migration on diagenesis and reservoir quality; Maracaibo Basin, Venezuela. American Association of Petroleum Geologists, *Bulletin,* **74:** 661.

Gonzalez de Juana, C. & Iturralde de Arozena, J. M. 1980 Geologia de Venezuela y de sus cuencas petroliferas, *Foninves,* **I-II,**1031pp.

Lander, R.H. & Walderhaug, O. 1999 Predicting porosity through simulating sandstone compaction and quartz cementation. American Association of Petroleum Geologists, *Bulletin* **83:** 433-449.

Lander, R.H., Felt, V., Bonnell, L. & Walderhaug, O. 1997a Utility of Sandstone diagenetic modeling for basin history. American Association of Petroleum Geologists and Society of Economic Paleontologists and Mineralogists Annual Meeting, *Abstracts,* **6:** 66.

Lander, R.H., Walderhaug, O. & Bonnel, L. 1997b Application of sandstone diagenetic Modeling to reservoir quality prediction and basin history assessment. I Congreso Latinoamericano de Sedimentologia., *Memorias,* **I:**373-386.

Lugo, J. & Mann, P. 1995 Jurassic-Eocene Tectonic Evolution of Maracaibo basin, Venezuela. IN: Tankard, A.J., Suarez, R. & Welsink, H.J. Eds. Petroleum of South America. *AAPG Memoir,* **62:** 699-725.

Lundegard, P.H. 1992 Sandstone porosity loss-A "big picture" view of the importance of compaction. *Journal of Sedimentary Petrology,* **62:** 250-260.

Oelkers, E.H. 1996 Physical and Chemical Properties of Rock and fluids for chemical mass transport calculations. IN: Litchtner, P.C., Steefel, C.I. & Oelkers, E.H. Eds. Reactive Transport in Porous Media. Mineralogical Society of America, *Reviews in Mineralogy,* **34:**131-182.

Parnaud, F., Gou, Y., Pascual, J-C., Capello, M., Truskowski, Y. & Passalacqua, H. 1995 Stratigraphic Synthesis of Western Venezuela. IN: Tankard, A., Suarez, R. R. & Welsink, H. Eds. Petroleum Basins of South America. *AAPG Memoir,* **62:** 682-698.

Perez, R.J. (1998) *Calidad como reservorio de la Formacion Misoa, Campo Bachaquero Tierra, Costa Bolivar, Estado Zulia.* Unpublished senior thesis. Universidad Central de Venezuela. 445pp.

Perez, R.J., Gomez, M. & Cassani, F. 1997 Integración diagenesis-petrofisica y calidad de reservorio, en un area de Rio Pauji, Zulia Oriental. *1st Latinoamerican Congress of Sedimentology,* **II:**165-172.

Platte River Associates 1995 Basic Training Manual of Basin Mod, Caracas, Venezuela.

Rodriguez, I., Navarro, A. & Ghosh, S.K. 1997 Nueva frontera exploratoria en la cuenca petrolifera del Lago de Maracaibo: Zulia oriental, Venezuela Occidental. VI Congreso Suramericano de Cuencas Subandinas. *Abstract.*

Roure, F., Coletta, B., De Toni, B., Loureiro, D., Passalacqua, H. & Gou, Y. 1997 Within plate deformations in the Maracaibo basin and east Zulia basins, western Venezuela. *Marine and Petroleum Geology,* **14:**139-163.

Walderhaug, O. 1994 Precipitation rates of quartz cementation in sandstones determined by fluid inclusion microthermometry and temperature history- modeling. *Journal of Sedimentary Research.* **A64:** 324-333.

Walderhaug, O. 1996 Kinetic modeling of quartz cementation and porosity loss in deeply buried sandstones reservoirs. American Association of Petroleum Geologist, *Bulletin* **80:** 731-745.