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ADVANCED CHEMISTRY BASINS MODEL TECHNICAL REPORT

- Covering the period from Dec 11, 2000 – June 10, 2001
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- Issued June, 2001

EXECUTIVE SUMMARY

The advanced Chemistry Basin Model project has been operative for 24 months. During this period, most project tasks are on projected schedule (up to 150% of goals). Of note are the scheduled tasks maturity indicators. On average the project is on schedule (100%). The goal of the past 6 months has been to get a prototype together by the end of this project year. As of this past week, all the pieces of the prototype have been demonstrated, and all communications between pieces have been tested. The final wiring of the prototype should be complete within the next several weeks, on target.

MILESTONE SCHEDULE/STATUS

The only milestone listed in the project is to have a prototype model operational on a workstation. Progress towards that goal has been substantial (as detailed below) and on schedule. In conformance with good software design requirements, the prototype has been designed modularly, in several pieces. Each of the pieces has been tested independently. With such a design, testing communications between the pieces becomes problematic, as the pieces are only weakly-coupled. These tests were satisfactorily completed at the beginning of this month. All that remains to fulfill the milestone is the final 'wiring-together' of the prototype sections, which should be complete by the end of June. What remains is to then incorporate all scientific results in the prototype, debug it, and improve usability.

TASK 1: MATURITY INDICATORS

Primary Responsibility	*Current Subtasks*	*Investigator*
Caltech	Develop algorithms	Tang

Summary: The first task is to "Develop a database of additional and better maturity indicators for paleo-heat flow calibration". Fundamental to this development is to perform a series of controlled kinetic experiments on maturity indicator evolution. The second year subtask is to "study R0 suppression, Compare thermal indicators, and Finish the R_0 Database". Future goals include:

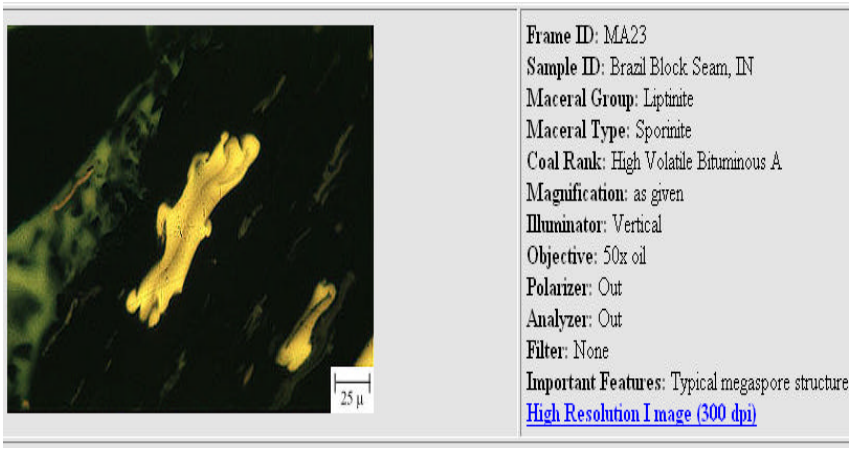
- Tie masceral (H/C, H/O) composition to Ro kinetics (year 3)
- Generate Pyrolysis GC data (Gas/Oil Ratio, Paraffin Distribution) (year 3)
- Complete proposed number of samples for the R_0 Database (year 4)

Maturation Indicies: Kinetic parameters were determined for the C_{29} 5α(H),14α(H),17α(H) sterane epimer ratio 20S/(20S + 20R), the 17α(H),21β(H) homohopane epimer ratio 22S/(22S + 22R) and the C_{29} C-ring monoaromatic (MA)/C_{28} ABC-ring triaromatic steroid hydrocarbon (TA) parameter TA/(TA + MA). Biological marker data used for these calculations were obtained from sedimentary basins with well-characterized burial and geothermal histories. The "EASY %R_o" kinetic model of Sweeney and Burnham (1990) was used for calibration purposes.

An investigative study of other maturity indicators commonly employed for the assessment of thermal histories of sedimentary rocks, including the methylphenanthrene index (MPI-1), smectite to illite conversion in shales and the thermal annealing of fission tracks in apatite, was initiated. Literature reviews have been started.

Vitrinite reflectance kinetics database: Vitrinite reflectance (R_o) kinetics have been determined for six (6) different kerogens. Pyrolysis experiments were carried out in sealed gold tubes at two different heating rates. As of the end of the second calendar year, we have accomplished about 50% of the proposed task. Method has been developed and tested in field conditions. Recent work includes developing kinetics for two vitrinite-rich coals. Planned future work includes a study of the variation of vitrinite reflectance for similar macerals, and to complete proposed number of samples for the R_0 Database. Information in the R_0 Database is of a form demonstrated by Figure 1

Deliverable 1:
Paleo-Heat Flow Calibration - Vitrinite Reflectance



Teerman and Tang, Unpublished Data

Figure 1: Vitrinite Reflectance data

Vitrinite suppression: R_o kinetics have been derived for liptinite-rich type II and type III kerogens. By combining R_o-temperature data for these two kerogen end members, we can now correct for vitrinite suppression in mixed type II-III kerogens.

TASK 2: COMPOSITIONAL MATURATION

Primary Responsibility	*Subtask*	*Investigator*
Caltech	Establish a reaction network	Tang

Summary: The second task is to "Develop maturation models capable of predicting the chemical composition of hydrocarbons produced by a specific kerogen as a function of maturity, heating rate,

etc.; assemble a compositional kinetic database of representative kerogens." For the second year of the project, the sub-task is to "Expand and Modify the reaction network developed in Year 1".

Gas generation from Kerogen: We have completed experiments on five different kerogen samples for gas generation using gold tube pyrolysis. Gas formation rates for C1, C2, C3, C4, CO2 and H2S have been quantified. The data will be used to calibrate our kinetic model for primary gas generation. Of interest to industry is the calculation of GOR (gas/oil ratio), or "gas proneness" of a kerogen. Experimental techniques can aid in this prediction, as shown by Figure 2.

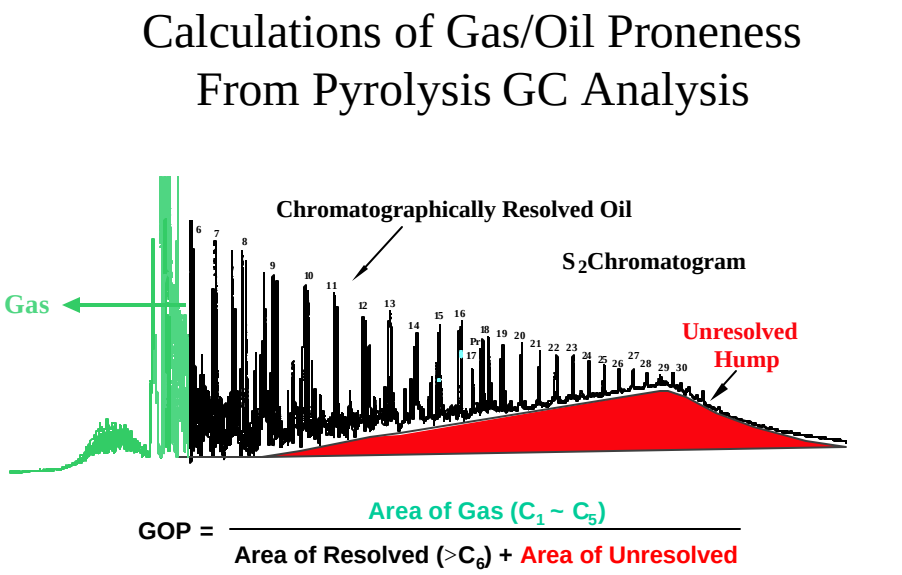


Figure 2

Hydrocarbon primary generation: We have evaluated both simple and complicated hydrocarbon generation models. A potential model has been developed, based on experimental work in part shown in Figure 3. The 13 member of hydrocarbon formation from our previous work have shown consistent results in terms of kinetic fittings. Still to be determined is the transfer function from compositional information into basin oil property prediction.

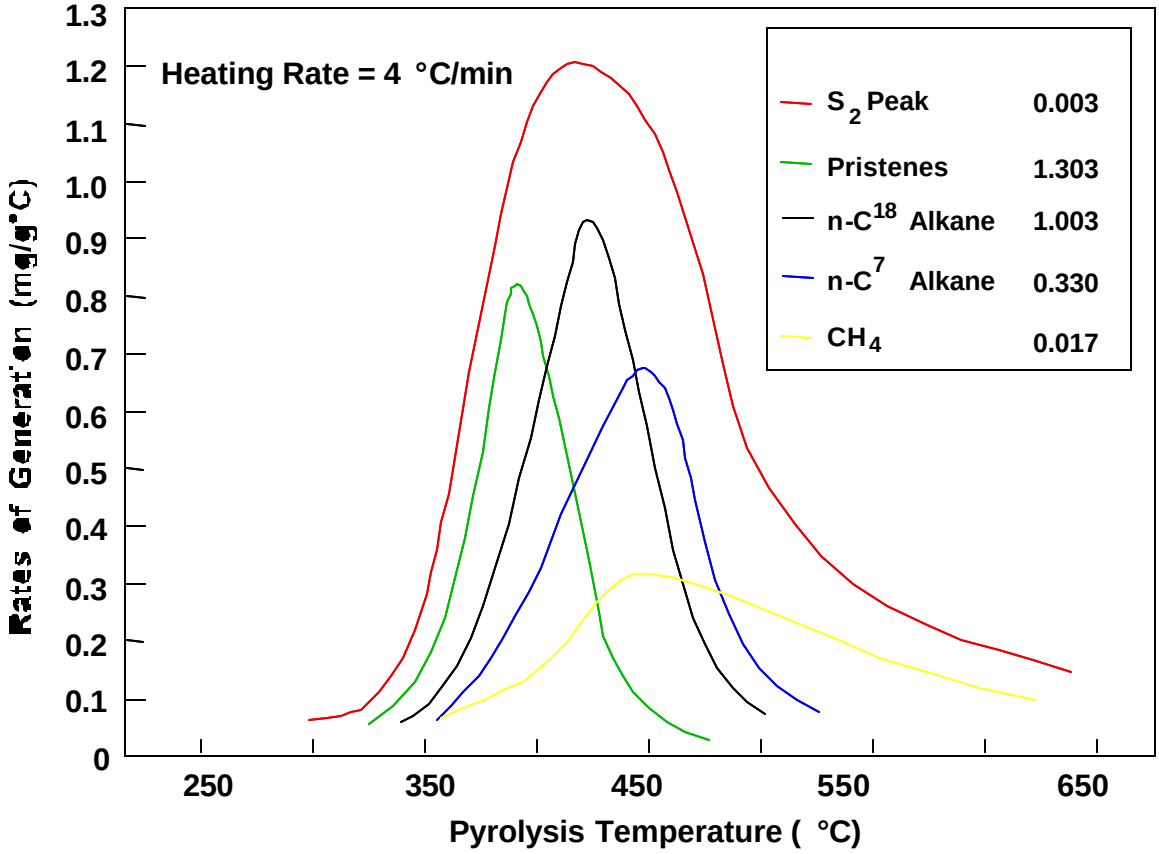


Figure 3: rates of Gas Generation

A particular emphasis of work has been to examine TSR (thermal sulfate reduction) of oils in reservoirs. Though a little outside of the purview of the original proposal, TSR has been generally recognized in the oil industry as being responsible for tremendous oil alteration, and any model that hopes to accurately predict chemical changes in oils during maturation and migration needs to be able to predict TSR.

Over the past 6 months, significant experimental work has been performed to understand the mechanism behind TSR. This work has shown that TSR results in:

- Enhancement of both methane and light hydrocarbon (C2-C5) production by a factor 2.
- Good correlation between hydrogen sulfide and methane production. In particular the correlation is excellent between H_2S and n-alkane production.
- A similar trend is found between hydrogen sulfide and light hydrocarbons (C2-C5) production.

- No correlation between H_2S and CO_2 / H_2 production

- TSR seems to occur on the surface of minerals, not in a water phase.

TASK 3: EQUATION OF STATE FLASH CALCULATION

Primary Responsibility	*Subtask*	*Investigator*
Caltech	EOS model	Meulbroek

Summary: The third task of the project is to "Develop a 4 phase equation of state-flash model that can define the physical properties (viscosity, density, etc.) of the products of kerogen maturation, and phase transitions that occur along secondary migration pathways." For the second year of the project, the sub-task is to: "Determine Henries Law coefficients controlling maturation product interaction with the aqueous phase, and develop a prototype of full computational scheme."

The two-phase equation-of state model previously developed in *Mathematica* has been ported to perl, a scripted, platform independent language that can communicate with the other pieces of the project. In the past 6 months, this new code has been adapted to use COM, a Microsoft technology that eases communication between programs. A database has been implemented to store properties of oil components. Currently, the model relies on a database of 1500 possible oil compounds. Communication protocols between the database and the EOS code have been implemented in a database-independent way, to allow individual users to connect to the database of their choice. It is envisioned that corporate users of this software will have their own databases that they will want to utilize.

The overall communications scheme has been developed for the prototype. After an initial solution, the prototype will communicate using a COM channel to the Flash model, passing sets of (p, t, z) information. The flash model will return two-phase compositions, relative volumes, and GORs (gas-oil ratio). As of the close of this reporting period, the model has been tested against literature data, and shows good agreement. The communications protocols have been tested, and seem robust. Still to be done is the final wiring. This has proven more difficult than originally anticipated, due to unforeseen incompatibilities between different Microsoft platforms (Windows NT and Windows 2000). These difficulties will be worked out within the next few weeks.

In principle, Henries Law coefficients can now be calculated. After reviewing methodology, a Henry's law methodology was rejected in favor of a three-phase flash calculation method (e.g., Prausnitz, 1986). This scheme will be implemented in the next year.

A pseudo-component-based viscosity model has been developed by the Tang group that requires very small sample sizes. This will be incorporated into the basin model during the next project year.

TASK 4: CONVENTIONAL BASIN MODELING

Primary Responsibility	*Subtask*	*Investigator*
Cornell	2-D model	Cathles
Cornell	add maturity indicators	Cathles

Summary: The fourth task of the project is to "Build a conventional basin model and incorporate new maturity indicators and data bases in a user-friendly way". For the second year of the project, the sub-task is to "test code, and incorporate additional kinetic data bases". This has been slowed somewhat by the unforeseen difficulties in other sections of the project (see the June 10, 2000 report). However, the progress towards a prototype has been on schedule, and an alpha-level prototype should be available by the end of this month, on schedule.

The conventional basin model is implemented except for erosion, where there is a bug in the NT code (a bug not present in the original Macintosh prototype). A great deal of work was expended (in the 3d half-year) to implement regridding schemes. Based on the results of tests performed with the new scheme, we have concluded the best approach for the DOE model will be grid refinement in the faults rather than re-gridding across the faults. This will simplify the models (from the user point of view) considerably. From a user point of view, regridding is just too complex, and there is no way to simplify the procedures. Our aim is to have a simple and easy to use advanced chemistry model that does not require an expert modeler to operate, so grid refinement seems the best option given the goals of the project.

Vitrinite reflectance maturity indicators are imbedded in the model. The framework for simple biomarker maturity indicators has been established and we are awaiting a trial R_0 database. However, based on developments discussed below, We now feel that organic indicators based on changes in oil chemistry may be best incorporated as part of the hydrocarbon chemistry modeling (see below).

TASK 5: PRIMARY MIGRATION

Primary Responsibility	*Subtask*	*Investigator*
Cornell	2-D model	Cathles
Cornell	prototype algorithm	Cathles

Summary: The fifth task of the project is to "Develop an algorithm which combines the volume change and viscosities of the compositional maturation model to predict the chemistry of the hydrocarbons that will be expelled from the kerogen to the secondary migration pathways." For the second year, the subtask is to "explore chemical feedback in primary flow". This algorithm has been implemented combining both traditional concepts of primary migration—that primary migration is a response to changes in volume due to hydrocarbon maturation—as well as the new concepts relating to capillary effects.

A prototype primary migration algorithm is complete, as reported previously. In the past six months, Yuling Zheng has since developed a stand-alone Matlab prototype version of the model with a windows interface. He will use this to scientifically explore the functionalities of the primary migration algorithm; especially how long the expulsion of oil may be delayed from time of maturation. This work will verify and extend the algorithms already in the DOE model, and point the way to their proper integration with the secondary migration algorithms. For now we will assume

that oil and gas migrate along secondary migration pathways as soon as they are produced in sufficient volumes to be mobile according to conventional relative permeability criteria.

The prototype will be encorporated into the existing code body in the next reporting period.

TASK 6: SECONDARY MIGRATION

Primary Responsibility	*Subtask*	*Investigator*
Cornell	Develop prototype	Cathles

Summary: The sixth task of the project is to "Develop an algorithm that predicts the flow of hydrocarbons along secondary migration pathways, accounts for mixing of miscible hydrocarbon components along the pathway, and calculates the phase fractionation that will occur as the hydrocarbons move upward down the geothermal and fluid pressure gradients in the basin." The first year sub-task is to "Develop prototype chemical advection algorithm linked to finite element models". An algorithm has been developed that includes migration based on buoyancy with migration based on pressure gradients.

A prototype secondary migration algorithm should be by the end of the fiscal year on schedule. Algorithms have been completed that deconstruct the bulk "oil" and "wet gas" components that are predicted by our previously-completed maturation models into the 40 or more oil components needed for a flash calculation. A stoichiometrically balanced oil decomposition model has been completed and joined to this maturation/deconstruction model. The dynamic link library protocols that are required to communicate hydrocarbon P-T-X data to a flash model are being developed. The flash model will return the molar volumes of the liquid and vapor (if any) phases. The migration algorithm will then redistribute the hydrocarbons until no element is over-filled, as described in the proposal. (see task 4).

TASK 7: INTEGRATION ON PC

Primary Responsibility	*Subtask*	*Investigator*
Geogroup	connect external code	Manhardt

Summary: The final task for the project is to "Integrate the above components into a functional model implemented on a PC or low cost workstation." For the first year, the subtask is to "Develop mechanism for connecting external C or FORTRAN algorithms into PC system and train others in the code requirements." This task has been satisfactorily completed. The code will be implemented on a PC running Microsoft Windows NT, and the different sub-programs will connect using ActiveX communication mechanisms.

Progress continues. Tests have been successful to date utilizing several cases from the US Gulf of Mexico. Testing and improvement of the new model on GOM basin data continues. The species migration model has now been verified for highly complicated grids that become quite distorted as the basin builds. In the absence of the availability of the developing chemistry model, the multiple species capability of the advection algorithm is being tested using available source models for lumped hydrocarbons and CO2. We expect validation of multiple species by early fall.

Appendix: The Prototype

The milestone for the first two years is to have a completed software prototype developed. Our interpretation of that mandate is to have an 'alpha' version of the code available. In the nomenclature of software development, an alpha version is the first release of a project. Significant features have yet to be added, and serious bugs still exist in the project, but enough of the project is functional for the user to get a feeling for the product's abilities. As mentioned above, the prototype is designed as a loosely-coupled set of modules, connected using ActiveX-COM communications. Software design experts agree that, when practical, loosely coupled modules are a better design than tightly coupled modules, as the loose coupling allows easier debugging and easier component reuse. As of the beginning of June, we have developed two modules: a fluid-phase-equilibrium module and a geological module. During the next calendar year, it is proposed that several additional modules will be included in the final product.

Fluid-Phase Equilibrium Model

As described under Task 3, above, an Equation of State-based FPE model has been adapted for this project. The model was ported to Perl during the last reporting period. This period, the perl components were compiled to a COM object, and tested in communication with Visual Basic (as a standard object broker). The module calculates results of user-specified flash calculations, using oils defined in a separate stand-alone database. Currently, the database is running under Microsoft Access. By the next reporting period, platform-independent database solutions will be tested.

Geological Module

A prototype geological model is now together. The prototype is written in APL. As of the end of the reporting period, COM communications with standard Microsoft tools (including Excel and Visual Basic) has been tested. Screen shots of the geological model are shown in Figure 4 and Figure 5.

The geological model is designed to utilize data in a number of different formats. At the lowest level, the user inputs an 'sflat' ("short, flat") file that incorporates physical geological data. An example of this file is shown in Figure 6.

Final wiring of the prototype is expected by the end of this months. Preliminary tests are very promising.

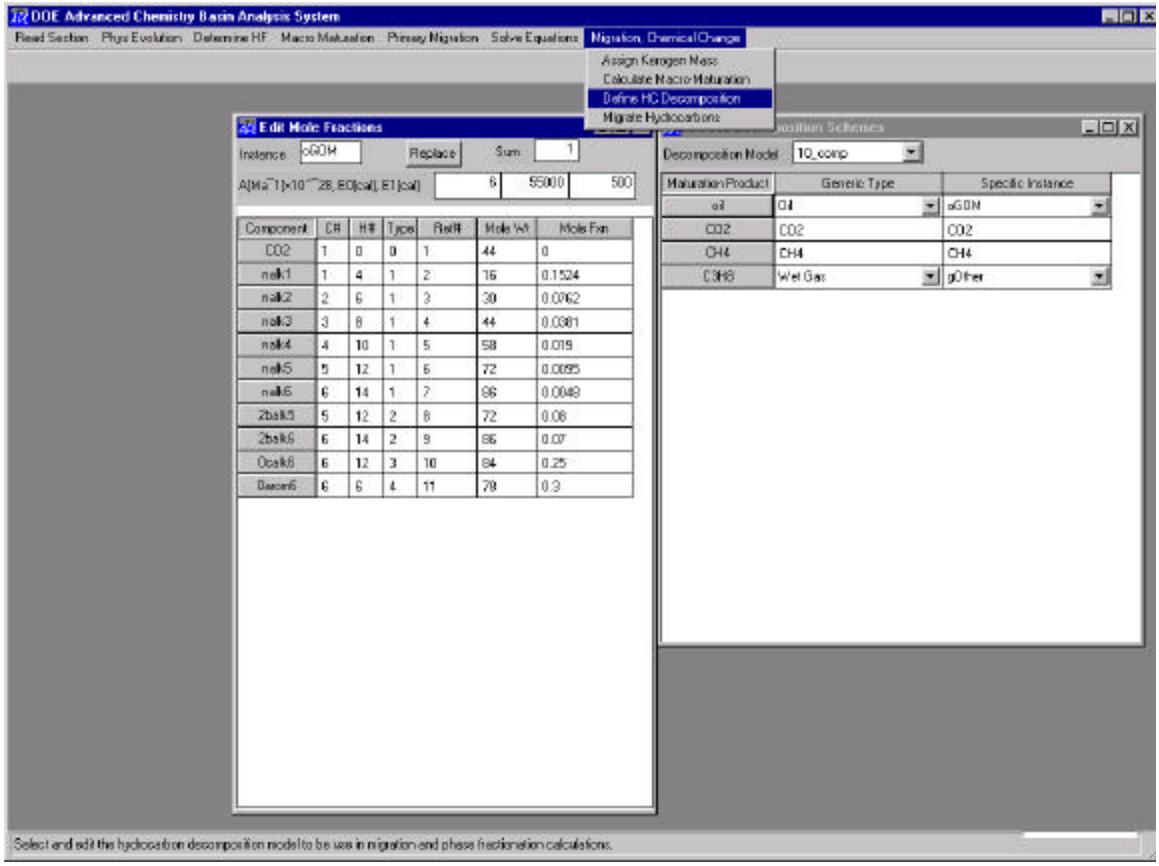


Figure 4: The Geological Model

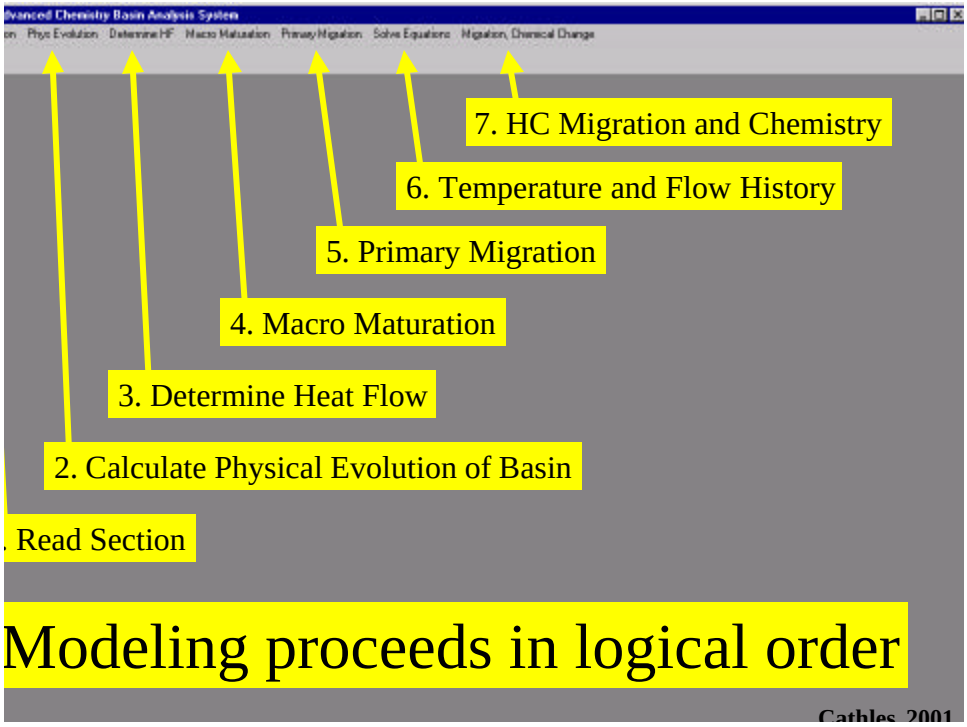


Figure 5: The Geological model in use

Example SFLAT Excel File

65	10	# Nbr Lines, Nbr Columns in sflat #								
5	0	#Nbr wells, linear(0) or exponential(1) compaction #								
5	13	# Nbr wells, Nbr Hrzns #								
1	1	# Scale x, Scale y #								
	W_Nbr	H_Nbr	X1	X2(depth)	Fx_Sd	Fx_Sh	Age(Ma)	Ker1(wtpct	Ker2(wtpct	HF(hfu)
Well_1	1	1	0	0	0	1	0	0	0	2
str_1ma	1	2	0	-0.5	0	1	1	0	0	2
str_2ma	1	3	0	-1	0	1	2	0	0	2
str_3ma	1	4	0	-1.5	0	1	3	0	0	2
str_4ma	1	5	0	-2	0	1	4	0	0	2
str_5ma	1	6	0	-2.5	0	1	5	0	0	2
str_6ma	1	7	0	-3	0	1	6	0	0	2
str_7ma	1	8	0	-3.5	0	1	7	0	0	2
str_8ma	1	9	0	-4	0	1	8	0	0	2
str_9ma	1	10	0	-4.5	0	1	9	1	0	2
str_10ma	1	11	0	-5	0	1	11	0	0	2
str_11ma	1	12	0	-5.5	0	1	12	0	0	2
str_12ma	1	13	0	-6	0	1	13	0	0	2
Well_2	2	1	10	0	0	1	0	0	0	2
str_1ma	2	2	10	-0.5	0	1	1	0	0	2
str_2ma	2	3	10	-1	0	1	2	0	0	2
str_3ma	2	4	10	-1.5	0	1	3	0	0	2
str_4ma	2	5	10	-2	0	1	4	0	0	2
str_5ma	2	6	10	-2.5	0	1	5	0	0	2

ADVANCED CHEMISTRY BASIN MODEL
FETC/Caltech/Cornell/GeoGroup

CORNELL UNIVERSITY
GeoGroup Inc.
Cathles, 2001

Figure 6: An example data file