EUG XI

Symposium FMF2

Rates of Fluid-Rock Processes and
Mass-Transfer during Deep Burial Diagenesis
in Sedimentary Rocks

Sponsored by BP – Amoco

Convenors

Stuart Haszeldine
Richard Worden
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Tuesday PM Session

FMF2 : TUpm25 : F4

Duration of Ore Genesis and Flux of Zn-Pb Mineralising Brines in the Cantabrian Basin, Spain

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The zinc-lead deposits at Reocin and La Troya, NE Spain are 200 km apart, differ in host lithologies and style of mineralisation but were common products of the same process. Serendipity and careful field observations have allowed almost-unique estimation of duration of emplacement and thus calculation of mineralising fluid flux.

Reocin contained 87 M tonnes resource (~11% Zn, ~1% Pb) emplaced in Late Aptian pinnacle reef limestone. Ore textures include karstic cavities containing sphalerite both as stalactites and laminated geopetal sediments alternating with clastics. The latter include allochthonous surface-derived quartz and lignite, introduced via karstic collapse. Sulphur isotope values show gross disequilibrium indicating rapid, low-temperature precipitation. Dolomite cement oxygen isotope compositions indicate 45 to 65ºC. All these observations indicate near-surface ore-emplacement. Palynology of internal sediments yields a mainly terrestrial, earliest-Albian assemblage. Ore emplacement was space-filling, occurring very rapidly after deposition, dolomitisation and karstification of reef limestones, restricted in time to one micro-fossil zone (~1 My). The amount of zinc is ~9.6 million tonnes giving a minimum metal flux of ~10 tonne per year.

La Troya is smaller, 3.3 M tonnes of ore (13.4% Zn, 1.1% Pb) of which nearly 75% is massive, bedded and occasionally laminated sulphide and the rest is in silicified carbonate. It appears to be of sedimentary exhalative origin, bounded by a fault, probably the hydrothermal vent. It overlies hydrothermally altered Aptian rudist-reef limestone and shale and is bounded above by unmineralised pyritic shale. Fluid inclusions and oxygen isotope values identify dense, 25% salinity, metalliferous brines emerging at >200ºC. Ore formed at 125 to 145ºC in an anoxic sub-basin by reaction with sulphide reduced from seawater sulphate. The laterally continuous unmineralised shales show the duration of ore emplacement was ~1000 years and of exactly the same age as Reocin. The Zn flux is 415 tonnes per year with a similar value for silica. Brine composition and temperature imply metal values that give a minimum one cubic Km. fluid volume and a minimum flux of one million cubic metres per year.

The genetic model for both deposits involves metalliferous brine formed in overpressured Triassic shales and carbonates sealed by thick Keuper evaporites. Tectonic tension and slightly increased heat flow caused halokinesis, producing diapirs, probably causing the structures on which reefs developed. Diapirism also thinned the seal allowing catastrophic release of ore fluids which escaped through faults around diapir flanks. These examples give rare measures of flux and duration for real ore deposits as opposed to MOR hydrothermal vent measurements which refer to a process contributing to a different type of deposit.

We acknowledge approval to publish from BP and Rio Tinto, but neither is responsible for the information or opinions presented here.

FMF2 : TUpm26 : F4

Rates of Hydrothermal Fluid Input in Sedimentary Basins – The Case of the Athabasca Basin, Saskatchewan (Canada)

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The Proterozoic Athabasca sandstones are the host of the giant high grade unconformity-type uranium deposits. These deposits are commonly hosted and surrounded by breccias controlled by basement-rooted and graphite-rich reverse structures (Lorilleux et al., 2000). Early pervasive silicification of sandstones dramatically decreased its permeability and favored the development of hydraulic brecciation triggered by a tectonic event between 1.52 and 1.25 Ga. The newly formed fractures in sandstone were percolated by silica undersaturated basement fluids, inducing breccia maturation by quartz dissolution and new formation of clay. Fractal analysis of breccia fragment morphologies indicate the predominance of slow dissolution in diffusion-limited regime over fast dissolution in kinetic regime (Jébrak, 1997; Lorilleux et al., 2000). Breccia textures show the occurrence of collapse phenomenons subsequent to the quartz dissolution. Collapse, developed up to 250 meters above the unconformity, led to the formation of hydrothermal karstification. The lower part of the karst at the unconformity is dominated by intense quartz dissolution whereas the upper part is dominated by collapse resulting from the dissolution below. The space created by quartz dissolution at the unconformity acted as a trap for the uranium mineralization. Mass balance calculations indicate that silica dissolution has been accompanied by important volume losses up to 90%. The very high fluid/rock ratios up to 38,000 in breccias occurring in the core of faults indicate percolation of huge amounts of fluids. The dissolution rates and the time of activity of the hydrothermal karst systems are dependant on the permeability variations of the fault system. The space created by quartz dissolution acted as a fluid feed back mechanism sustaining the permeability and enhancing the dissolution rates by fast renewal of undersaturated fluids. Collapse and clay mineral cementation subsequent to the quartz dissolution acted as self-sealing factors.

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FMF2 : TUpm27 : F4

A Dissolution and Precipitation Model for Fluid Flow in Geological Media

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Many processes in the Earth's crust are controlled by the chemical and physical interactions between fluids and the geological medium. These include economic mineral deposition, hydrocarbon migration, diagenesis and earthquake genesis. To accurately model these processes any numerical scheme must consider heterogeneous permeability, mineral dissolution and precipitation and the feedback between these reactions and the fluid flow. There is abundant evidence that the dominant factors in governing fluid flow, fault networks and rock permeability, obey fractal statistics which are heterogeneous in nature. The dissolution/precipitation of rock minerals and chemical transport alter the rock properties which leads to a change in the flow characteristics and the geological media through time. To model fluid flow in heterogenous media we use a modified Lattice Boltzmann (LB) method which is a discrete method for modelling fluid flow. The scheme facilitates the incorporation of complex boundary conditions and enables us to examine fluid flow in heterogeneous media. In addition, the local update rules of this scheme allows the code to be parallelized on multiple processors. Using this scheme we have incorporated reactive flow and transport of chemical species. Experimentally derived dissolution/precipitation rates are used to calculate rates of interaction between minerals and the fluids with which they are in contact. We have modelled laboratory scale dissolution experiments from the literature to check our reaction rates and transport of chemical species. We intend to apply the code to several geological scenarios including the temporal evolution of aquifers, resevoirs and fault networks by examining the changes in porosity, mineral compostion and fault networks. The LB method is easily extended to three dimensions and we are currently upgrading the scheme to 3D. Recent advances in the LB method will also allow us to incorporate thermal driven flow.

FMF2 : TUpm28 : F4

Spatial and Temporal Variation of Chemical Composition of Deep Groundwaters in Sedimentary Basins

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The chemical composition of groundwaters is influenced both by physical (transport, dispersion) and chemical (dissolution, exchange, diffusion..) processes. The groundwaters in deep sedimentary basins are characterised by long residence times, complex and variable mineralogical compositions of the matrix and the existence of several aquifer/aquiclude layers. In this paper, our approach is to compare theoretical calculations, including aquifer/aquiclude interactions with field observations issued from literature studies. This leads to the following remarks:

• if we compare the velocity of mass transport with the kinetics of dissolution, it can be assumed that this last process does not play a significant role for the considered minerals;
• in theory, the various dissolution mechanisms of minerals present in an aquifer should generate concentrations which unfortunately do not often correspond to measured concentrations;
• some minerals, such as calcite or mica, are characterised by alteration times in the order of several tens of My justifying by this way their ubiquity in such aquifers;
• ion exchange can play a significant role in two cases: (i) when the velocity of groundwater is low, and (ii) when the nature of clays located in the aquiclude is favourable.
• in consideration with geological times, diffusion from an aquiclude can be a major process and can affect the chemistry of the aquifer as a whole;
• leakage from an aquiclude generates coupled hydraulic head and concentration gradients which should be stable over time.
•The vertical heterogeneity of the aquifer should have a minor impact on groundwater composition, as long as the low permeability layers are thin compared to total aquifer thickness. This type of approach may help, jointly with field measurements and paleohydrology, eustatism, and structural information, to understand which processes best explain the observed water chemistry in a given aquifer.

FMF2 : TUpm29 : F4

Does Anhydrite Dissolution Control the Rate of Thermochemical Sulfate Reduction?

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Thermochemical Sulfate Reduction (TSR) is a process observed in some gas and oil reservoirs above temperatures of about 120-145°C. Above these temperatures, petroleum compounds such as methane are destroyed by reaction with anhydrite to form calcite, H_2S and other minor components. TSR consists of a variety of more elementary steps, including dissolution of mineral and gaseous reactants, and diffusion to the point of reaction, geochemical interaction in the aqueous phase and mineral precipitation. Since determination of the TSR kinetic mechanism from field or experimental studies remains difficult, we propose to use a reaction-transport modeling approach (Le Gallo et al., 1998) to gain insight into the rate-controlling mechanism of TSR. Ideally, the model should be able provide explanations for several observations including the high minimum temperature of reaction, the extent of the reaction as a function of depth, and the coexistence of anhydrite and petroleum even in reservoirs where TSR is at an advanced stage. Although the intrinsic rate of anhydrite dissolution is very high (Barton and Wilde, 1971; Dove and Czank, 1995; Cross et al., 1997; Bildstein et al., in press), we suggest that the actual rate of dissolution might be limited by the diffusion of aqueous reactants through a calcite armoring (Bildstein et al., in press). Indeed, textural evidence indicates that calcite precipitates on the outer edge of anhydrite nodules leading to a progressive isolation of the remaining anhydrite from the petroleum phase (Worden and Smalley, 1997). Reactants must therefore diffuse through a very tortuous, low porosity armoring, which results in a dramatic decrease in the anhydrite dissolution rate. We calculated a diffusion coefficient appropriate for this calcite armoring to be six orders of magnitude smaller than that in free water. As TSR proceeds, the anhydrite nodule progressively dissolves away and the thickness of armoring increases (through a 'shrinking core' model). This, in turn, increases the diffusion path length of the reactants. With this model, the simulations predict the completion of TSR (i.e. destruction of the initial 5% anhydrite) in 200,000 years (at 170°C) to 300,000 years (at 120°C). The simulation results match closely the observed trend of reaction extent as a function of depth in the Khuff Formation reservoirs (Worden and Smalley, 1997) for temperature higher than 140°C. These results would be compatible with TSR lasting 25,000 to 100,000 years in the Khuff Formation. At lower temperature, however, the model tends to overestimate the extent of TSR, thus suggesting that TSR is controlled by the rate of aqueous redox interaction between sulfate and petroleum at lower temperature rather than the rate of 'diffusion-controlled' dissolution of anhydrite.

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FMF2 : TUpm32 : F4
Kinetic Rates Constrained by well Documented Field Examples and the use of Geochemical Modelling: The Example of Carbonate Kinetics and Sherwood Sandstone Aquifer (UK)

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Water-rock interaction is controlled by the stability domains of minerals, kinetic rates of dissolution and precipitation, and water composition and flow velocity. As regards kinetics, large discrepancies have been noted between rates derived from laboratory experiments and rates inferred from observations of natural systems. Examples that are sufficiently well documented to provide constraints on mineral kinetics are rather rare.

For this presentation I used published data for the Sherwood Sandstone (Triassic) aquifer (East Midlands, UK). The distinct compositional zonation in the aquifer, has been interpreted as the consequence of coupling between water movement and mineral reactions (Edmunds *et al*., 1982). I used a reaction-transport numerical model, Diaphore, to simulate the water-rock processes acting in the aquifer. As the model integrates kinetics, the simulation of this case study could provide a constraint on the kinetics of calcite and dolomite, which are present in the aquifer. Model inputs included : i) water-flow rate constrained by isotopic dating of the groundwaters (Bath *et al*., 1979) ; ii) composition of the groundwaters (Edmunds *et al*., 1982) ; and iii) mineralogical composition of the sandstone (Edmunds *et al*., 1982). Three zones were distinguished along a ~30-km transect from outcrop, where water infiltrates the aquifer. They correspond to progressive reaction fronts governed by the hydrodynamic regime. Zone I has recent water (<1,000 years) which dissolves dolomite. Zone II has waters dated at 1,000-10,000 years, which dissolve dolomite and precipitate calcite. Zone III has waters dated at 10,000-35,000 years, which are closer to carbonate equilibria and which are enriched in sulphate possibly derived from gypsum or anhydrite. Diaphore was used to reproduce the observations (water and rock compositions in the three zones). The minerals considered were quartz, Na-rich plagioclase, K-feldspar (orthoclase and microcline), muscovite, biotite, illite, haematite, goethite, calcite and Fe-rich dolomite. The contribution of pyrite, and of gypsum/anhydrite, in parts of the sedimentary formation, was also tested. The simulations solve the mathematical conservation equations of the elements Si, Al, Na, K, Ca, Mg, Fe, C, O, H and Cl (eventually, S).

The geochemical model catched unambiguously reactions involving carbonates. It was used to evaluate to what extent these reactions are coupled : i) to O_2 reduction, occurring in Zone I (partly Zone II), and interpreted as an effect of Fe(II) release by Fe-rich dolomite (Edmunds *et al*., 1982) ; and ii) to other redox processes occurring when the sulphur minerals are considered. On the other hand, kinetic rates of carbonate reactions are discussed in terms of intrinsic rate and reactive surface area.

As far as industrial applications are concerned, such well documented case studies are extremely useful to control the precipitation rates of minerals considered as potential sinks of CO_2 and other greenhouse gases.

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FMF2 : TUpm33 : F4
Experimental Study of Diffusional Mass Transport and Phase Transformations in a Thermal Gradient at Low Temperature

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Water-rock interactions and mass transport controlled by the spatial variation of temperature are fundamental processes in geothermal sites or radioactive waste deposits. Our purpose is to identify the influence of this thermal gradient on the dissolution and precipitation rates and on the mass of matter transferred by the aqueous phase. Several tube-in-tube experiments were conducted in the Si-Al-Na-K, the Si-Al-Mg, and the Si-Al-Mg-K system. In those experiments solid phases are located at the extremity of a gold tube filled with water (Vidal, 1997). Thermal profile from 300°C to 200°C is imposed along the tube. After 40 days to 90 days, the walls of gold tubes are examined with a SEM to observe which minerals precipitated during the run. The distribution of the newly formed products cristallizing from the solution provide information 1) on the dissolution processes of the starting material located at the extremity of the tube, 2) on the diffusional mass transport between the starting products and newly formed ones, and 3) on the temperature stability conditions of the newly formed phases.

In the Si-Al-Na-K system (granite powder or feldspath + quartz starting mixtures at the hot extremity), the following sequence was observed toward the cold extremity: quartz, feldspars and then alkaline and calcium clays. The experimental results are in good agreement with the numerical simulations made with KINDIS and THERMAL softwares (Made and al, 1990; Jacquot, 2000), which suggests that our experimental design is appropriate to predict the long-term evolution of geothermal sites such as the HDR geothermal site of Soultz-sous-Forets. The clays newly formed in the experiments showed a variable composition along the tube. The type of experiment performed enabled us to have the chemical composition of the clays with regard to the temperature. It is a valuable method to find the relations between temperature and chemical composition, which is difficult to obtain as such low temperatures. The clays are evolving from a potassic pole at high temperatures to a sodic pole at low temperatures. The experiments in the Si-Al-Mg±K system show that the quantity of matter displaced by diffusion is closely related to the direction and the magnitude of the thermal gradient. The following sequence was observed: saponite, vermiculite, or chlorites at the hot extremity (depending on the chemistry of the starting material) and kaolinite, illite or beidelleite at the cold extremity of the tube. We can then find some phase relations which had not been studied in these temperatures (Aja and al, 1991).

Each experiment definitely shows that aluminium is mobile in aqueous phase at these temperatures and for an important fluid / solid ratio. Aluminium cannot be considered as the immobile element in these conditions.

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FMF2 : TUpm34 : F4
Cross Formational Flux of Aluminium and Potassium in Gulf Coast Sediments

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Many studies of sandstone and shale diagenesis have identified potential imports or exports of elements present in cements (e.g. Wilkinson and Haszeldine, 1996). It is usual for workers studying sandstones to presume that the external solutes are sourced from shales, and vice-versa. Very few studies look at both sandstones and shales, and attempt to quantify solute transfers. That fluid transfer occurs is undeniable - hydrocarbons undoubtedly migrate from shales into sandstones.

Whole-rock geochemical data from the Frio formation of the USA Gulf Coast are available for both sandstones and enclosing shales (Milliken et al., 1994; Land et al., 1997). Graphs of 'mobile'/'immobile' element ratios show a statistically significant relative decrease of K (mobile) with depth for sandstones, and a corresponding increase relative to Ti, Zr, and Hf (immobile) in shales (Wilkinson et al., 2000). We interpret this as indicating that K is exported from sandstones to shales during deep burial. This is consistent with recent studies in the Gulf Coast and Mahakham Delta, where K import into shales has been demonstrated. Data for Al is also suggestive of a net flux from sandstones to shales, though of marginal statistical validity. Assuming that the sediment had an initially uniform chemical composition, then K (and probably) Al are exported from sandstones into shales, despite the common assumption of Al immobility. There is insufficient export of K from sandstones to account for the import of K into shales, so another source of K must exist. However there is probably Al-conservation within the Frio Formation, as the calculated outflux from the sands and the influx from the shales approximately balance. The sandstone data set has more scatter than that from the shales, suggesting that the problem of Al mobility could be better addressed by a larger sandstone data set: more data are required to conclusively settle the question of Al mobility.

The volumes of clay minerals precipitated within a sandstone may be controlled not only by reactions taking place within the sandstone, but also by reactions within the surrounding shales. As authigenic clay minerals, and especially illite, dramatically reduce sandstone permeability, this conclusion has obvious predictive implications for hydrocarbon reservoirs. If the transport of solutes from sandstones into shales is not a spatially uniform process, but occurs preferentially in certain areas (determined by fluid flow patterns), then these areas become potential targets for the oil industry. As fluid flow, driven by overpressure, is concentrated into structurally favoured regions (termed leak-points; e.g. Wilkinson et al., 1997), then these regions have less volume of reaction products (i.e. permeability-reducing authigenic clays) than would be predicted using a closed-system diagenetic model. Importantly, these areas will have higher porosity and permeability than the regional norm for their burial depth.

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FMF2 : TUpm35 : F4
Dickite after Major Corrosion during Deep Burial Diagenesis of Carbonates: Evidences of Fluid Chemistry Changes and Mass Transfer

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The carbonate platform sequences of the studied Cenozoic reservoirs suffered extensive obliteration of primary or early diagenetic porosities during progressive burial. Intermediate to deep burial diagenesis was dominated by pressure-dissolution and associated carbonate cement precipitation. The $\delta^{13}C$ and $\delta^{18}O$ values of successive stages of carbonate cementation suggest a normal burial trend of increasing temperatures and evolution of interstitial brines mixing with basin-derived compaction fluids. In addition, this cement sequence detects the sporadic influx of organically-derived CO_2, probably sourced from coal intercalations in volcanoclastic deposits below the carbonate sequences.

A major corrosive event caused dissolution of any preceding carbonate cement as well as micrite matrix. The flow pattern of corrosive mixed fluids was controlled by faults, fractures, main unconformities, grainstone layers and an intricate network of horizons of pressure dissolution,tension gashes and stylobreccias. Micro and macroporosity (up to cavern size) developed as result of the main corrosion event.

Dickite cements, together with minor amounts of pyrite, gypsum, fluorite and barite, partially filled cavities formed during the major corrosion stage. Dickite was externally sourced from the site of precipitation, probably originated from the volcanoclastic sediments below. The paragenetic evolution, from progressive cementation during the burial trend to major corrosion and cavity formation followed by dickite precipitation, suggests significant changes in the fluid chemistry. Moreover, the presence of dickite cements in these carbonate rocks prove the participation of processes favoring the mobilization of Si and Al.

The major corrosion is explained as a result of mixing corrosion by two different fluids: (i) a deep-seated evolved meteoric aquifer in the basal volcanoclastics (up to 160ºC, $\delta^{18}O$ up to +8‰ and $\delta^{13}C$ from 0 to -20‰ and (ii) the formation fluids (up to 80ºC and $\delta^{18}O$ around +1°/₀₀ with variable $\delta^{13}C$ from +3 to -20‰). The nature and isotopic composition of the post-corrosion precipitates add valuable constraints on the post-corrosion diagenetic environments. Carboxylic acids derived from maturation of organic matter in the volcanoclastics might have played a major role in dickite mobility. The significance of organic-matter related diagenesis and bacterial sulfate reduction is shown in the $\delta^{34}S$ values of pyrite and gypsum. δD and $\delta^{18}O$ of dickite suggest the modification of meteoric fluids due to rock-water interaction at high temperatures.

The irruption of the deep-seated aquifer appears to have been triggered by a change on the regional stress. This together with the peak maturation and migration of hydrocarbons played a major role in the generation of pervasive corrosion during deep burial and helped in the transfer of Al and Si from the basal volcanoclastics to the carbonates. The continuous supply of meteoric waters to the deep-seated aquifer might have been a key factor for Al and Si transport.

Tuesday PO Session

FMF2 : TUpo01 : PO
Characterizing the Boron Isotopic Signatures in Clay-Marl Deposits (Callovo-Oxfordian, Meuse, France) by High Resolution IMS

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The Callovo-Oxfordian clayey layer is the potential host rock for reconnaissance work carried out by ANDRA in eastern France, in order to design and to build an underground research laboratory to study the aptitude of a sedimentary setting for the storage of radioactive wastes. Within the framework of the programme to determine present and past groundwater circulation conditions having affected the reconnaissance site, a methodology based on the interpretation of chemical and isotopic data ($^{87}Sr/^{86}Sr$, Rb, Sr, ^{18}O, ^{13}C) recorded in the carbonates and the clay minerals, was applied to core samples from the MSE101 and HTM102 boreholes (Casanova et al., 1999). The present study is an attempt to test the feasibility of boron isotope measurements in carbonate and clay materials in order to separate the continental influence from the marine signature, if any. The clay formation lies between two carbonated units. The footwall of the clay formation, is made up of Bathono-Callovian oolitic to gravelo-bioclastic facies that are an equivalent of flaggy Bathonian limestone. The top wall unit, appears to be made up of Oxfordian micritic then biohermal limestone. High mass-resolution $^{10}B/^{11}B$ analyses were performed on 15 samples from the HTM 102 borehole, using a Cameca IMS 1270 ion-microprobe according to the analytical procedure described by Chaussidon et al. (1997). A reference was run (standard GB 4, $\delta^{11}B = +12.8 \pm 0.5‰$) and the 13 $\delta^{11}B$ values ranged from -13.6‰ to -11.3‰ leading to a mean value of -12.79 ± 0.5‰ (2σ±). In order to avoid the influence of the epoxy resin signal, the data obtained with less than 10000 Cps (i.e. content > 1 ppm) were not considered. The boron contents, estimated by Cps, fluctuate largely from 1 to more than 15 ppm. Fluctuations are observed both along the sedimentary column and within individual samples. Most of the high boron contents have been recorded within the argillites whereas the less concentrated analyses correspond to carbonates. This range of boron content is in agreement with parallel investigations by ICP-MS on bulk leacheates (Casanova et al., 1999). Based on samples where epoxy influence is negligible, the $\delta^{11}B$ fluctuate largely ($-20‰ < \delta^{11}B < +17‰$) and these variations can be analysed through a classical mixing diagram ($\delta^{11}B$ vs. 1/B). The highest $\delta^{11}B$ and B contents are assumed to correspond to the carbonates. A second end-member characterised by negative $\delta^{11}B$ values and high B contents may correspond to clay minerals, resulting of continental crust weathering and erosion. Marine clay minerals display an intermediate $\delta^{11}B$ signature together with a lower B content. A detailed investigation (HTM621, 353-m level) reveals large fluctuations in B contents (1.7-15.8 ppm) and B isotope composition ($-19.09‰ < \delta^{11}B < +16.77‰$) and highlights the heterogeneous nature of the sedimentary matrix.

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FMF2 : TUpo02 : PO
Characterisation and Sealing Abilities of Non-Reservoir Chalks of the Central North Sea

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As part of the Geosciences Project into Overpressure (GeoPOP) the characteristics of 'non-reservoir' Chalk of the Central North Sea have been investigated to establish if Chalk lithologies can act as a pressure seal.

Twenty five samples were characterised using a number of techniques (including petrological analysis, porosity and pore size distribution and permeability measurements) to establish if a particular facies or formation were dominated by low permeabilities or whether low permeability rocks were pervasive throughout the Chalk Group.

Petrological studies have revealed that clean (non argillaceous) Chalks undergo a relatively simple diagenetic transformation with mechanical compaction being limited due to a framework of grains resisting compaction. Chemical compaction is also simple, principally consisting of overgrowth cementation and grain to grain pressure solution. In contrast the diagenetic history of argillaceous Chalks is more complex with extensive mechanical compaction occurring, in addition to irregular cementation and widespread dissolution. A similar interpretation could be derived from pore size distribution as clean Chalks show a gradual reduction in mean pore size with depth while argillaceous chalks show constantly small mean pore radii (5-20nm).

Permeability measurements were also conducted using the Transient Pulse Decay method, which is capable of measuring extremely low permeability (down to 0.01 nannoDarcys). The method has been previously used for siliciclatic mudrocks but this is the first time this method has been applied to Chalk.

Permeability measurements show that most non-reservoir Chalks have low permeabilities (typically of 10s of nannoDarcys) irrespective of depth (2000-3900 m), clay content, facies or formation. The only exception is where inclined stylolites are present, suggesting that locally stylolites can act as fluid pathways.

This suggests that the non reservoir Chalks can act as a significant barrier to fluid flow and can act as significant pressure seals within the North Sea Central Graben.

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Fluid Circulation during the Tectonic Evolution of the Foreland Basin of Khenifra, Massif Central, Morocco: Preliminary Results from Field Observations

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Fluid circulation during the sedimentological, postsedimentary and tectonic evolution of a flexural basin changes successively the permeability and the porosity of the sedimentary rocks, thus ameliorates or detoriates the quality of hydrocarbon or water reservoirs. It has also an influence on the capacity for industrial or radioactive waste disposal. The objectives of our project are to study the nature and the modification of the cementation pattern in the sedimentary units of the NNE-SSW orientated flexural basin of Khenifra. It is mainly filled with Carboniferous flysch, carbonates, siltstones and black shales. Field studies along a cross-section in the northern part of the basin indicate that the Variscan orogeny led to ductile deformation, thrusting and intercalation of Devonian turbidite facies sheets within the Upper Viseen (UV) sequence. Fracturing occurred during folding and thrusting, as well as post orogeny. Four major phases of fluid circulation were recognized at present in both, the UV flysch sediments and carbonates, and the Devonian sediments. Fluids I are of synsedimentary origin or are released during compaction, normal synsedimentary faulting or slumping. They led to the formation of carbonate nodules in UV and Devonian black shales and to the precipitation of iron oxides nodules in Devonian sandstone. Sandstone banks within UV flysch or Devonian turbiditic sediments show evidence of syncompactional fluid generation ±perpendicular to So in form of millimetric sized quartz veins and, minor, calcite veins. Fluid phase II, generated during folding and westward thrusting, was injected parallel to S1 (N10-40/45-85 SE). Fluid phase III is related to thrusting and cristallized quartz which are characterized by kinkbands indicating a later deformation. Post-or synorogenic fluids IV cristallized in fractures, faults, diaclases and horizontal displacements of two major directions: 1. N 120/either dipping to the SW or to the NE, 2. N60/50-60 NW or SE (conjugate faulting). The latter direction is consistent with the regional direction of the microgranite dykes known in the southern part of the basin. Several centimetre wide fractures and diaclases are mainly filled with coarse sparitic calcite. Ironoxides and hydroxides coprecipitated locally.

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Estimates of Fluid Flow from In Situ Pore Pressure Measurements in the Continental Rise West of the Canary Islands

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In 1995 and 1996 several measurements of the in situ pore pressure using the PUPPI (Pop Up Pore Pressure Instrument) (Schultheiss, 1990) were carried out on the continental rise west of the volcanic island of La Palma, in water depths ranging between 4000 and 4500 m. The apparatus, deployed at radial distances from the island of between 60 and 120 km, showed negative equilibrium pressures at most sites of up to -85 Pa. Compressibilities and permeabilities were calculated from the half decay times of the insertion pore pressure and the amplitudes of the tidal pore pressure variation respectively, which allowed calculating seepage velocities within the sediment. These seepage velocities show negative, although low (up to -0.3 mm/yr), values in accordance with the observed pore pressures, while classical passive margins are characterised by an upward fluid flow mostly conditioned by sediment compaction. The results are thus interpreted as the superposition of a volcanic related hydrothermal cell to the flow regime of the passive margin. The complex pore pressure gradients derived from the equilibrium pore pressure profiles at each site also suggest the horizontal migration of fluids through layers of contrasting permeability.

Schultheiss PJ, *Marine Geophysical Researches*, **12**, 153-168, (1990).

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Quantifying Carbonate Precipitation in a Carbonate Ramp using Sulfur Isotopes and a Diffusion, Advection, Reaction Model

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The continental margin of South Australia is characterized by a huge quaternary carbonate ramp, which is considered a modern analogue of many Mesozoic carbonate ramps. The interstitial waters recovered during ODP Leg 182, are characterized by a complex system of mainly seawater-derived brines with chlorinities up to 1.5 M. Together with the relatively high organic matter content of the carbonates (up to 0.8wt%), this stimulates intense sulfate reduction and carbonate dissolution/precipitation. The observed alkalinity values exceed 120 mM. Based on the measured properties, chlorinity, sulfate and sulfide concentration and isotopic composition, we developed a numerical model of sulfate reduction and alkalinity production. First results from Site 1130 show that under the assumption that no anaerobic methane oxidation occurs, alkalinity production rates may exceed 0.6 mM per second and cubic meter at a depth of 25 mbsf. Using this numbers as input into a diffusion advection reaction model, and fitting the reaction term against the measured alkalinity, allows for the determination of the carbonate dissolution/precipitation rates.