

EUG XI



Symposium FMF4

Sulphur Geochemistry and Gases in Geofluids
during Burial Diagenesis and Metamorphism

Convenors

Kurt Bucher
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FMF4 Sulphur Geochemistry and Gases in Geofluids

Tuesday AM Session

FMF4 : TUam01 : F4 Radon Concentration in a Deep Sedimentary Aquifer from the Aquitaine Basin (Southwest France)

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In deep aquifers, groundwater geochemistry and isotopes measurement are useful tools in addition to geological and hydrogeological information to access aquifers behaviour. Isotopes measurement are used to assess residence times and to determine the origin of waters. Moreover isotopes like radon can provide information about local conditions of flow. This paper concerns ^{222}Rn measurements in a deep sedimentary aquifer (Eocene sands) situated in the Aquitaine Basin (Southwest of France). Radon measurements were made using two methods:

- Instantaneous measurement in gas phase, after groundwater degassing;
- Continuous measurement (1 week) at some places to access radon variability during pumping. In the studied area ^{222}Rn concentration range from 4 to 90 Bq/L, with an increase in the north east part. In the central area radon concentrations range from 4 to 10 Bq/L and in the north-east part there is a more important gradient from 10 to 90 Bq/L. Such variations can be attributed to the composition and origin of the sediments (i) deltaic and marine origin in the central part (ii) continental origin in the north-east part, to groundwater flow pattern and/or to vertical communication between aquifer and aquiclude. Radon concentrations will be the result of two fluxes:
- One from the Eocene sands, with difference between central on north-east area;
- Another one from clay layers (above and/or in the aquifer), this contribution can be more important for regions where the sand layers are thinner. Such observations can be used to provide a better understanding of water-rocks interaction and to constrain a hydrodynamic flow model.

FMF4 : TUam02 : F4 Helium Behaviour and Residence Times in Water-Rock Systems in Northern Switzerland

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To study residence times of rare gas isotopes in rocks and related aquifers or pore gases, concentrations of U, Th, Li, K, and He and Ar isotopes were measured in ~150 sedimentary and metamorphic rock samples and mineral separates, collected mainly from NAGRA test sites, Switzerland. The measured rare gas concentrations were compared with the calculated values, which would have been yielded in-situ assuming no loss/gain of species of interest. This comparison shows that generally rocks and related groundwaters have almost completely lost radiogenic in-situ produced He, implying that the water/rock system has not been a closed system since the time of sedimentation, and that movable waters have removed helium: only <10% (down to 0.1%) of He produced has been retained in a water-rock system. The overall inventories of He isotopes show that their external sources are not required. Providing local sources, helium production rates together with measured abundances of He in pore fluids allow crude estimates for residence times of movable He in pore space, generally within ~10 to 0.1 Ma. The principal assumption behind these estimates, steady state accumulation/loss of radiogenic species, stands in need of special investigation. There are interesting exceptions from this generalisation. One of these relates to Permian sandstones from the Molasses basin: the rocks contain more ^3He and ^4He than could have been produced. $^4\text{He}/^3\text{He}$ production ratio calculated for the sandstones, 7×10^7 , is by a factor of 6 above these measured in the rocks, 1.2×10^7 . The latter is quite similar to the production ratio in the adjacent shale aquitard, 1.4×10^7 , and also to that observed in Permian groundwaters, 1.1×10^7 . These data suggest generation of

both helium isotopes in shales, their migration to the sandstone aquifer, and lastly He penetration into vehicles in quartz and feldspar crystals, carriers of trapped excess He in the sandstone. This suggestion is further confirmed by enhanced U, Th and Li concentrations in shales, so that these rocks are the principal source of helium isotopes in the Permian shale-sandstone interlay, and by almost complete loss of both radiogenic helium isotopes, >90%, by the shales. Occurrence of trapped helium in rocks, which have almost completely lost in situ produced He, was also observed in some other localities. In chemical sediments discrepancy between observed and production $^4\text{He}/^3\text{He}$ ratios could be due to different behaviour of helium and tritium in damage tracks yielded by emission of these nuclides.

FMF4 : TUam03 : F4 Crustal Fluids in Mantle Rocks: The Noble Gas Composition of Proterozoic Lamproites from the Eastern Baltic Shield

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Noble gas isotopic data represent a powerful tool to distinguish between crustal and mantle derived fluid components. Here we present results of noble gas investigations of early Proterozoic lamproites (whole rock and mineral separate samples) from the eastern Baltic Shield (Kostamuksha/Karelia craton), performed by stepwise heating and crushing. K-Ar dating of mica and kfs yields an age on 1223 ± 13 Ma, in good agreement with Sm-Nd and Rb-Sr ages (1235 Ma, Belyatskii et al., 1997). K-free minerals (cpx, quartz, carbonate) reveal the presence of excess argon which was also found in a fluid inclusion component, released by crushing. As shown by distinct gas release temperatures, ^{40}Ar and ^{36}Ar are coming from different locations. We suppose fluid inclusions as the main reservoir of ^{36}Ar , because ^{40}Ar as a product of decay of ^{40}K is generated in the crystal matrix. It can be shown that diffusion of ^{40}Ar from the matrix into the fluid inclusions is negligible. Therefore, an external fluid phase is most likely the source of the excess argon. Neon and helium isotopic data help to clarify the origin of the fluid component. The Ne isotopic ratios of crushed samples display a mixing between air and a crustal component (Kennedy et al., 1990), when plotted in a three-isotope-diagram. Neon stepwise heating data additionally show the presence of nucleogenic ^{21}Ne and ^{22}Ne , produced in situ by Wetherill reactions $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ and $^{19}\text{F}(\alpha, n)^{22}\text{Ne}$. $^3\text{He}/^4\text{He}$ ratios of crushed samples and of U/Th-poor minerals are indistinguishable from the crustal ratio ($1 - 4 \times 10^{-6}$). In melted whole rock samples and U/Th-rich minerals, they are in good agreement with those calculated for (n, α)-reactions in ^6Li (Mamyrin and Tolstikhin, 1984). Therefore, if there had been any mantle-originated fluid phase in these rocks it was overprinted by another fluid component with crustal origin.

Belyatskii BV, Nikitina LP, Savaa EV & Levsky LK,
Geochem. Int., **35**, 575-579, (1997).
Kennedy BM, Hiyagon H & Reynolds JH, *Earth Planet. Sci. Lett.*, **98**, 277-286, (1990).
Mamyrin BA & Tolstikhin I, *Helium Isotopes in Nature Elsevier*, 273 pp, (1984).

FMF4 : TUam04 : F4 Gas Monitoring at Geothermal Exploration Well GPK-2 (Soulz-Sous-Forêts, France) – First Results from the 5000 m Production Test

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The knowledge on the chemistry of deep crustal fluids is essential for the evaluation of the exploitation potential of geothermal energy resources. Hereby, the concentration and composition of gases dissolved in the brines is an important parameter. For example, dropping pressure

causes degassing which may become dangerous if combustible gases will be released. Degassing may also lead to serious technical problems because of the formation of two-phase fluids and the precipitation of solid matter and scaling. In cooperation with Socomine/BRGM we monitored in real-time the water and gas flux as well as the gas composition of the "5000 m brine" at the GPK-2 well in Soulz-sous-Forêts, France, during the 1999 production test (cf Baria et al., 1999). For detailed analyses of trace gases and noble gas isotope ratios off-line gas and fluid samples were collected from the gas separator and from the casing outflow line for laboratory investigations at the GeoForschungsZentrum Potsdam (GFZ).

We determined in real-time fluid temperatures, fluid flow, gas fluxes in the casing and behind the gas separator at the rig platform as well as N_2 , CO_2 , Ar, H_2 , He, CH_4 , and O_2 every minute with a portable quadrupole mass spectrometer. In average the "5000 m fluid" salinity is 90 g/l (NaCl dominated) at 40°C and pH 5.5. The submersible pump was installed 125 m below the rig platform. The drawdown pressure was at least 12 bars at a flow rate of about 20 l/min. The rising formation fluids were degassing partly before reaching the pump, this fraction of gas (roughly 10-20%) entered the open casing volume. The remaining gas phase was mostly liberated by the gas separator. The "casing gas" and the "separator gas" compositions were significantly different, so that the less soluble gases (e.g. N_2 , He) were relatively enriched in the casing gas phase. Thus, either gas phase does not represent the true formation gas composition. Combining the compositions of these gas fractions and considering the composition of fluids totally degassed in the laboratory, the following average gas composition for the "5000 m fluid" was calculated on an oxygen free basis: $\text{CO}_2 = 89.5$, $\text{N}_2 = 7.3$, $\text{H}_2 = 1.7$, $\text{CH}_4 = 1.2$, Ar = 0.2, and He = 0.1 (all values in vol%) at a water to gas ratio of 2.5. According to the helium isotopic compositions the majority of the gases are of crustal origin, however, they indicate 4% of mantle-derived helium, which is in perfect agreement with earlier investigations on spring and deep well fluids from this region (Griesshaber et al., 1992).

Baria R, Baumgärtner J, Gérard A, Jung R & Garnish J,
Geothermics, **28**, 655-669, (1999).
Griesshaber E, O'Nions RK & Oxburgh ER, *Chem. Geol.*, **99**,
213-235, (1992).

FMF4 : TUam05 : F4 Origin of Large Volumes of Carbon Dioxide in Sedimentary Basins: A Case Study from the Cooper Basin, Australia

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Collated stable carbon isotope analyses from sedimentary basins around the world suggest that large volumes of carbon dioxide in petroleum reservoirs come from outside the petroleum system ($\delta^{13}\text{C}$ ratios are 0 to 10‰). The mantle is one possible source for such carbon dioxide and mixing of one or more sources is, of course, possible. In order to investigate such sources rare gas isotopic (^3He , ^4He , Ar) and stable carbon isotopic abundances have been measured on carbon dioxide-rich gases from the Cooper Basin. The Permian age Cooper Basin has undergone a complex history of structural deformation and has experienced periods of both extension and compression. The gas reservoirs studied range in depth from 1900 m to 3000 m and are hosted in three fluvio-deltaic, coal-bearing sandstone sequences.

Methane is present (up to 80 vol.%) and has a $\delta^{13}\text{C}_{\text{CH}_4}$ signature of -42 to -28‰ PDB. Such isotopic values indicate a thermogenic source for the methane, with the thermal cracking of coal being the most likely source.

Stable carbon isotopes suggest that large volumes of CO_2 (up to 50 vol.%) are multisourced. Isotopic signatures range from -4 to -15. $\delta^{13}\text{C}_{\text{CO}_2}$ PDB. CO_2 could be sourced

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from Permian age coal sequences, as well as from igneous sequences. Carbon isotope ratios have been interpreted with rare gas ratios to distinguish these sources.

FMF4 : TUam08 : F4 Organic Compounds in Volcanic Gases

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A large range of organic compounds emitting from volcanoes have been detected significantly above atmospheric background concentrations, using novel analytical techniques. The majority of the organic compounds have not been previously reported from volcanic emissions. Our results from different sites in the Mediterranean, Kamchatka and New Zealand provide for the first time directly quantified data on compounds including short chain alkanes, alkenes, arenes, and halogenated and sulfonated derivatives (e.g., HCF₃'s, CFC's, perfluorocarbons). For some compounds (CH₂Cl₂, CHCl₃ etc.), concentrations are several orders of magnitude greater than present-day atmospheric backgrounds, and above midlatitudinal industrial urban air maxima. The importance of volcanic halocarbon emissions to stratospheric chemistry is that their negligible aqueous solubility does not lead to a quantitative tropospheric wash-out effect as for volcanic HCl and HF emissions.

Sampling and analysis of organic compounds in volcanic gases have to be customized to the difficult matrix of volcanic discharges. All previous attempts have two major analytical problems in common: improper sampling techniques (loss and reaction of compounds by photolysis, catalysis, oxidation, and reaction with condensate), and insufficient gas-chromatographic separation: high sulphur, water and mineral acid backgrounds shielding and eliminating organic signals. We successfully developed and applied *Short-Path Thermal Desorption-Solid Phase MicroExtraction-CryoFocussing-High Resolution GasChromatography-Mass Spectrometry* (SPTD-SPME-CF-HRGC-MS) as a reliable standard protocol, together with new sampling techniques. This meets the required analytical accuracy for quantitative sampling and analysis, and for externally standardised direct quantitation. As a result of the increased sensitivity of our new method, halocarbon concentrations in volcanic gas emissions are found higher than previously estimated. This is of fundamental importance to the understanding of the global volcanic halogen flux, since previously volcanic organic emissions have been insufficiently quantified by using COSPEC-measured SO₂-emissions, which are known to be erroneous by not discriminating other aerosol particles (dust, vapor).

Among the detected quantified compounds are dioxins and furans, chlorophenols, phenanthrene; polyhaloalkanes (e.g. trichlorofluoromethane, CFC-11), methyl bromide, 2,2-difluoropropane (HFC-272), dichloromethane (R-30), chlorobenzene, and thiophene. Based on the large range of isomers detected, we deduce these compounds to have been synthesized by gas-phase reactions in an ascending gas column together with subsequent abiogenic alkylation, halogenation, and sulfidation, reactions. Although the roles of surface catalysis by mineral surfaces at high temperatures are still poorly known, the organic distributions observed are interpreted as high temperature (e.g., 9001°C) alkyl free radical reactions, and halide electrophilic substitution on arenes.

In order to ensure a primary magmatic origin of the organic compounds, gas source characteristics have to be defined. Source reservoir processes such as multiple source mixing and transport of waters and gases in volcano-hydrothermal systems are now understood in conjunction with noble gas systematics and other volatile species. We explain major chemical differences of across-island arc waters and gases in terms of relative ages of crustal magmatic heat sources and their replenishment.

FMF4 : TUam09 : F4 Potential H₂S-Controlling Mineral Reactions in Hydrocarbon Reservoirs

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The occurrences of hydrogen sulfide (H₂S) in hydrocarbon reservoirs has received considerable attention in deep carbonate systems, where high concentration levels may reduce the economic viability. Controlling reactions appear to involve anhydrite and hydrocarbon species (specially methane). In clastic hydrocarbon reservoirs hydrogen sulfide levels are normally much lower and less is known about the origin and controlling mechanisms.

The concentrations of H₂S in clastic hydrocarbon reservoirs from the Norwegian Shelf (Håland et al. 1999) and the US Gulf Coast (Smith 1997) exhibit a steady increase with burial depth and temperature. Various potential mineral reactions which may control the H₂S level have been explored and compared with the reported H₂S abundancies. These buffers were calculated based on the general geochemical control on burial diagenesis discussed previously by Aagaard & Egeberg (1998).

The computations applied the thermodynamic data base and the SUPCRT92 computer program of Helgeson and coworkers and also utilised the carbon dioxide trend of Smith and Ehrenberg (1989) from the Norwegian shelf. The redox conditions were evaluated following the approach and arguments of Helgeson et al. (1993), where the oxygen (and hydrogen) fugacity is assumed to be buffered by the acetic/pyroponic acid equilibrium. All calculations were done along an average North Sea P-T-gradient, taken from Smith and Ehrenberg (1989). Organic acid data of from North Sea oil field brines were used. The resulting O₂-fugacity follows a trend between the hematite-magnetite and magnetite-pyrite-pyrrhotite buffers. A corresponding H₂-fugacity was also established.

Giggenbach (1980), in his work on gas abundancies and distribution in hydrothermal systems in New Zealand, advocated equilibria between aluminosilicates and iron containing silicates to be active. We have tested out various silicate buffers for our clastic diagenetic systems, specially the pyrite-kaolinite-chlorite buffer, as well as pyrite /Fe-carbonates pyrite-magnetite buffer. It appears that the observed H₂S concentrations are buffered by iron sulfide-carbonate assemblages within the reported variation of the FeCO₃ component. This behaviour contrasts the anhydrite containing reservoirs which may produce high level of H₂S by reactions with hydrocarbons.

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FMF4 : TUam10 : F4 Bacterial and Thermochemical Sulfate Reduction in Diagenetic Settings- Old and New Insights

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Bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) appear to occur in two mutually exclusive thermal regimes. BSR is common in diagenetic settings from 0 up to about 60 to 80 °C. TSR is common in geologic settings with temperatures of 100 - 140 °C, but in some settings temperatures of 160 - 180 °C are necessary. BSR is geologically instantaneous, whereas rates of TSR are much lower, but still geologically significant. TSR may form sour gas reservoirs and/or MVT deposits in several tens of thousands to a few million years in the temperature range of 100 - 140 °C.

BSR and TSR may be exothermic or endothermic, depending mainly on the presence or absence of specific organic reactants. However, if the reactions are exothermic, the amount of heat liberated is very small, and this heat usually dissipates quickly.

The main organic reactants for BSR are organic acids and other products of aerobic or fermentative biodegradation. The main organic reactants for TSR are branched and n-alkanes, followed by cyclic and mono-aromatic species, in the gasoline range. Sulfate is derived almost invariably from the dissolution of gypsum and/or anhydrite.

The products of BSR and TSR are similar, but their relative amounts vary widely and are determined by a number of locally variable factors, including availability of reactants, formation water chemistry, and wettability. The primary inorganic reaction products in both thermal regimes are H₂S(HS) and HCO₃⁻ (CO₂). Common by-products are calcite, dolomite, various metal sulfides, and/or native sulfur. Water and porosity may be generated during TSR under certain circumstances, but neither appears to be common or likely. TSR can take place in fairly narrow reaction zones, where the irreducible water saturation in the hydrocarbon-containing pores is low. However, where the irreducible water saturation is high, TSR may take place throughout the entire hydrocarbon-containing pores volume. Solid bitumen may form as a by-product of both BSR and TSR.

The mere presence of any of the above reaction products and by-products does not permit a distinction between BSR and TSR. However, a number of petrographic relationships and geochemical criteria can be used to discriminate these two processes. Gas chromatography, carbon and sulfur isotope analyses, and/or a combination thereof, offer the best distinguishing geochemical criteria.

FMF4 : TUam11 : F4 H₂S in North Sea Oil Fields: Importance of Thermochemical Sulphate Reduction in Clastic Petroleum Reservoirs

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H₂S in North Sea basins is broadly limited to the Central and Wytch Ground Grabens where it occurs at concentrations of up to 20,000 ppm. To define the origin and controls on H₂S, oil and gas geochemical data, sulphur and carbon isotopic data from oil and reservoir data (including: temperature, pressure, reservoir lithology, gas-oil ratio) have been integrated for fields and wells covering the whole of the North Sea. H₂S is likely to be due to thermochemical sulphate reduction that occurred in reservoirs between sulphate-enriched waters, derived from Zechstein evaporites, and oil. Although the sulphur content of oil decreases with increasing reservoir temperature, H₂S and the oil-sulphur content are not inversely correlated: H₂S cannot have originated from S-compound cracking in oil. Moreover, while the nitrogen content of the bulk oil decreases with increasing oil maturity, the sulphur content does not decrease systematically suggesting that there is competing desulphurisation (through cracking) and sulphurisation (through back-incorporation of reactive H₂S). There is a positive correlation between the sulphur isotope ratio of oil and H₂S concentration again suggesting that TSR-H₂S has been incorporated into the oil. Enrichment of the oil in 34S is accompanied by enrichment in 13C signifying that the reacting oil is undergoing carbon isotope fractionation, once again typical of thermochemical sulphate reduction. H₂S is only notably enriched in oil fields at about 120°C. This confirms previous studies of the conditions under which TSR can occur in oil fields (i.e. at a slightly lower temperature than TSR in gas fields) and confirms that bacterial reduction is unlikely. H₂S is highly enriched only in Upper Jurassic, clean quartz arenites (and typically absent or at low concentration in the less clean Triassic, Middle Jurassic and Tertiary reservoirs). This suggests that in subarkosic and sublithic sandstones, TSR potentially has occurred but the H₂S has been scrubbed by Fe-minerals producing diagenetically late-stage pyrite cement, common in many North Sea reservoirs.

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Experimental Determination of Thermochemical Sulphate Reduction (TSR) Reaction Kinetics

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High concentrations of H₂S in petroleum gas and oil fields are attributed to Thermochemical Sulphate Reduction (TSR) reactions. H₂S is toxic, corrosive towards production steels, commonly associated with high carbon dioxide concentrations and consequently low hydrocarbon concentrations. High H₂S concentrations may affect the economic viability of a gas or oil field. TSR reaction kinetics have been determined in laboratory simulations at formation water pH.

TSR experiments have been performed in the sodium sulphate, acetic acid, sodium acetate and elemental sulphur system, at temperatures between 100 and 350°C. Sodium sulphate was used as an appropriate experimental analogue for anhydrite. Fluid-sampling hydrothermal pressure vessels were used, with which pressure and temperature could be controlled independently up to 50 MPa (500 bars; 7500 psi) and 350°C. The reactants were held within a gold reaction cell, with titanium closure and exit tube which leads to an external titanium sampling valve. Fluid samples were taken periodically to monitor reaction progress without quenching the reaction vessel to room conditions.

The rate law for the temperature dependence of the TSR reaction rate (min⁻¹) between sodium sulphate, acetic acid and sodium acetate, in the presence of elemental sulphur is:

$$\text{Log } k = -7.42(10^3/T) + 8.46$$

Kinetic data suggest that TSR occurs rapidly on a geological time-scale at relatively low temperatures (150°C). Sulphate half-lives are 15 days at 300°C, and 1650 years at 150°C. The activation energy of the reaction is 142 kJ/mol. Fluid pH increases by up to one unit during these reactions.

The TSR reaction rates reported here are significantly lower (1-2 orders of magnitude) than those reported by Kiyosu and Krouse (1990, 1993). Their data were established from experiments performed with similar reagents, but at pH = 1-2 and since the TSR reaction consumes H⁺ ions it may well be catalysed by acidic conditions. Goldhaber and Orr (1995) report comparable reduction rates, but at significantly lower temperatures, in experiments performed in the presence of H₂S. Hoffmann and Steinfatt (1993) conducted experiments with the same reagents (albeit in different concentrations) and reported a final pH = 6. Therefore, Goldhaber and Orr's experiments did not benefit from the catalytic effect of low pH. This suggests that H₂S is a more effective reaction initiator/catalyst than elemental sulphur. Goldhaber and Orr's data and the data from this project converge at high temperature, and diverge at low temperature. Compared to S, H₂S becomes increasingly effective as a catalyst as the run temperature decreases. This suggests that H₂S may be considerably more effective in catalysing the reaction at reservoir temperature than elemental sulphur.

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FMF4 : TUam13 : F4

The Origin of Pyrite-Acid Volatile Sulfide (AVS) Cross-Over Plots in Sediment Profiles

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Depth analyses of iron sulfides in modern sedimentary sequences commonly display profiles of pyrite increasing with depth and acid-volatile sulfides decreasing with depth. These cross-over plots appear to suggest that acid volatile sulfides transform in situ to pyrite in sediments. However, there are two major problems with this interpretation: 1. The mass balance FeS + (S) = FeS₂ (where FeS represents AVS, (S) represents addition of a sulfur species and FeS₂ is pyrite) does not balance. 2. The process is kinetically rather than thermodynamically controlled. The rate of transformation of FeS to pyrite *in situ* would then be a function of the surface area of the FeS. The surface area of FeS is approximated by the mass of FeS and thus rate = f[FeS]. This would imply that the rate of pyrite formation would increase with increasing AVS concentration which appears to be the opposite of that observed in the cross-over plots.

Studies of the kinetics and mechanisms of pyrite formation have demonstrated that pyrite forms from AVS via a dissolved phase (Rickard and Luther 1997). In the simplest case, the newly formed pyrite is not directly in contact with the precursor FeS and thus the Fe and S components must be transported from FeS site to the site of pyrite deposition. This has subsequently been shown to be consistent with the process of pyritisation of plant cells (Grimes *et al.*, in press).

The nature of the dissolved iron sulfide phase has been discussed in the literature. Davison *et al.*, (1999) have suggested an Fe (bi) sulfide complex whereas Theberge *et al.*, (1999) provided evidence that it is a FeS cluster complex. We refer to this as FeS_{aq}.

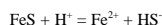
The dissolved iron sulfide phase, FeS_{aq}, has been detected experimentally. Rickard and Luther (1997) showed that it was present during pyrite formation from precursor FeS, and recent data from our group has demonstrated that the suppression of FeS_{aq} leads to inhibition of pyrite formation.

The FeS_{aq} species has also been detected in oceanic and freshwater systems. In a recent study of an estuarine sediment, Rickard *et al.*, (1999) demonstrated that the amount of pyrite formed was directly proportional to the concentration of FeS_{aq}.

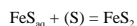
The conclusion of these studies is that the formation of pyrite from AVS in sediments involves a dissolved phase FeS_{aq}. In effect, AVS dissolves



and



and pyrite forms



The net result is that the sulfide mass exchange in the cross-over plots will not balance, since AVS is not transforming stoichiometrically to FeS₂. A dissolved phase is being produced, resulting in recycling of Fe and S.

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Grimes ST, Brock F, Rickard D, Davies KL, Edwards DE, Briggs DEG & Parkes RJ, *Geology*, in press, (2001).

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FMF4 : TUam14 : F4

Sulfur Isotopic Composition in Groundwaters from the Aquitanian Basin

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In sedimentary basins deep groundwater flow is complex and can be assessed only by the joint use of geological, hydrogeological, geochemical and isotopic data. This work has been engaged since several years on the "Sables Inframolassiques" (Eocene sands) aquifer. Two major areas having different geochemical patterns and piezometric levels are identified. The origin of such regions can be attributed to the composition of the sediments, horizontal circulations, or vertical communications. Sulfur isotopes (³⁴S/³²S), coupled to oxygen ones (¹⁸O/¹⁶O), help to determine the origin of waters and the main biogeochemical reactions. The analyses on rocks and water samples from the Eocene sand aquifer lead to the following observations: - Dissolved sulphates isotopic ratio (³⁴S/³²S) in the major part of the basin are similar to the one of gypsum found in mud layers above the aquifer. Analyses of oxygen isotopes in dissolved sulphates agree with an evaporitic origin of the sulphates. - Bioreduction is observed at the eastern boundary of the aquifer, H₂S concentrations reaching several mg/L. These values agree with the measurements of redox potential in formation waters. - In this area the sulphate isotopic ratio is highly negative (-1.63 to -20.12 permil) suggesting oxidation of pyrite. A simple model mixing dissolved sulphate from gypsum and from pyrite oxidation is able to reproduce the observed data. This emphasises the role of communications between aquifer and aquiclude and of the sedimentation conditions in the acquisition of groundwater composition. Beside, these results help to constrain the flow pattern at the basin scale.

Tuesday PO Session

FMF4 : TUp01 : PO

Thermogenic Hydrocarbons Associated with Active Hydrothermalism in the Bay of Plenty, New Zealand

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High-temperature (~200°C; water pressure-controlled boiling point) hydrothermal gases emerge from the shallow (180-200 m deep) seafloor near White Island and the Calypso vent site in the Bay of Plenty, New Zealand. The gases contain large amounts of CO₂ (72-84 vol.%), lesser CH₄ (6.2-9.9 vol.%) and minor amounts of the higher gaseous hydrocarbons C₂H₆, C₃H₈ and i-, n-C₄H₁₀ (739 to <1 ppm by volume). The composition of the submarine gases closely resembles that of fumarolic gas from crater-hosted vents on the active White Island volcano (e.g., Noisy Nelly). Carbon isotope values (δ¹³C) of the venting CO₂ are in the range -3.4 to -5.5 ‰ PDB, and are indicative of a relatively shallow (~1 km) magmatic carbon source. The δ¹³C values of the CH₄ fall in the range -24.6 to -28.9 ‰ PDB, and their δD values of -122 to -135 ‰ SMOW agree well with other published isotopic analyses of CH₄ from the Bay of Plenty. These isotope analyses together with the presence of higher gaseous hydrocarbons require a mixed thermogenic and abiogenic origin for the venting hydrocarbons. A first-order model based on the isotope data and published He-isotope values suggests magmatic gas comprises ~50% of the venting gas. However, this model is too simple. High-temperature maturation processes are revealed by the very positive δ¹³C values of ethane (near -20 ‰ PDB), and variations in gas geochemistry reflecting high-temperature maturation of sedimentary organic substances are to be expected. Long-chained hydrocarbons impregnate dredged volcanic rocks and sediment close to the active vent sites. Analysis of the n-alkane distribution reveals a high to moderate odd-even predominance, which is a characteristic indicator of higher land plant waxes in the organic source. Furthermore, the hopane series distribution provides evidence of bacterial life in the source. The transition from aliphatic- to aromatic-dominated bitumens, which is marked by the occurrence of substantial amounts of unsubstituted polyaromatic hydrocarbons, is consistent with extensive maturation resulting from increasing thermal stress. Therefore, the bitumens found on the seafloor probably represent mixtures of immature organic matter (i.e., a source close to the seafloor) and pyrolysates from the various thermal regimes at greater depths. In summary, the liquid hydrocarbons and a significant proportion of the gaseous hydrocarbons in the Bay of Plenty were generated by thermal maturation of organic materials. The source is probably a mixture of detrital terrestrial-derived material and drowned near-coast vegetation that developed during low sea-level stands.

FMF4 : TUp02 : PO

Seeping Hydrocarbons and Related Carbonate Mineralization in Sediments South of Lihir Island (New Ireland Fore Arc Basin, Papua New Guinea)

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Hydrocarbon gases have been sampled from both cold seeping and hot venting areas in the New Ireland fore arc basin in the vicinity of Lihir island. Highest concentrations of up to 10 μl/l CH₄ with a δ¹³C_{CH₄} value of -54.9 ‰ PDB have been measured in the deep ocean water within a long and narrow deep sea basin located between Edison

seamount and a horst structure named "Mussel cliff". Surface sediments of the seep area were covered with chemoautotrophic deep sea fauna like Calyptogenia species and tube worms. Large authigenic calcite concretions occur in the sediments between 50 and 200 cm sediment depth. The stable carbon isotopes of the carbonates in the concretions range from -15 to -40 ‰ PDB indicating a mixture of two CO₂ sources: normal marine-inorganic carbon fixed in biogenic shells and CO₂ from anaerobic oxidation processes of methane. Accordingly, ¹⁴C-AMS dating suggests that authigenic calcite mineralization incorporated relatively "young" carbon from methane oxidation. In contrast the C1/C2 ratio of 235 and the δ¹³C_{CH₄} value of -24.1 ‰ PDB in the hot hydrothermal vent of Lihir harbour indicates a mixture of a major abiogenic carbon source for methane formation related to magmatism associated with Lihir volcano. The observed variable fluid characteristics within only a short (20 km) distance between hot hydrothermal venting and the methane seeping deep sea area indicates highly variable heat flow situations and/or sediment distributions which control the gas geochemical characteristics in the New Ireland fore arc basin.

FMF4 : TUp03 : PO

Gas Monitoring of an Artesian Water Well in the Arava Rift Valley, Israel

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Within the scope of an international geophysical research initiative (DESERT 2000) we carried out a monitoring experiment at the ZOFAR 20 water well in the Arava Rift Valley, Israel, which is located near the main fault system of the Dead Sea Rift. The artesian well discharges 150 m³ of saline water per hour at 50°C. In static conditions the well head pressure is 2.1 bar. The well is 1017 m deep and completely cased. Between 830 and 1005 m, 10 sections are perforated in Lower Cretaceous sandstones. The main objective of the field experiment was to monitor variations in fluid chemistry and to correlate with local seismicity.

In cooperation with the Geological Survey of Israel we analysed in real-time fluid temperatures, well-head pressure, fluid flow as well as the gas flux and composition, following gas separation. We determined continuously during 50 days N₂, CO₂, CH₄, Ar, He, H₂, and O₂ with a portable quadrupole mass spectrometer as well as pH, conductivity and radon every minute at a constant water flow of 1500 l/h. For detailed analyses of trace elements and isotopic composition off-line fluid and gas samples were taken, regularly. The average salinity of the NaCl dominated crustal fluids is 6500 mg/l at 36°C and pH 7.3. The average gas composition on an oxygen free basis is 97 vol% N₂, 1.2 vol% CO₂, 1.1 vol% Ar, and 0.15 vol% He. Deviations from the average composition are less than 1% for N₂, 5% for He and Ar, and 25% for CO₂, respectively. These variations are most probably due to variable air temperature, and thus degassing efficiency. The ³He/⁴He isotopic composition of approx. 0.5x10⁻⁶ is clearly different from pure crustal-derived helium and demonstrates the existence of a mantle-derived helium component. Oxygen isotopes vary between -8.8 and -9.0‰ δ¹⁸O (SMOW) which is in agreement with other investigations in that region. So far, we could not confirm a clear relationship between physical or chemical fluid properties and artificial or natural local seismicity. Further trace element and isotopic data will be presented and discussed in the geological context.

FMF4 : TUp04 : PO

Are There Fluid Sinks within the Earth's Crust?

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Deep groundwater in fractured crystalline basement has been reported from deep mines and from scientific deep wells. Highly saline brines (Na-Ca-Cl) have been described from several km depth in the continental basement of the Canadian, Fennoscandian and Ukrainian shields and elsewhere in the world. In the Black Forest area, which represents a part of the central European continental crust, TDS of typical Na-Cl-type groundwater is more than 5 g/kg at a depth below 2-3 km. pH is in the range of 6 to 8. Groundwater composition indicates that dissolution of the major components of basement rocks, feldspar and mica, essentially dominate the chemical evolution of the waters and that the reaction with the granitoid rock matrix is the major source of cations. Black Forest deep waters are typically thermal waters with a marine signature. The relationships of water compositions were depicted on stability diagrams (activity-activity diagram) for relevant low-temperature phases at quartz saturation. The widespread occurrence of zeolite minerals in basement rocks is consistent with calculated phase diagrams that predict zeolites as reaction products from feldspar alteration. The essential mechanism that generates the observed groundwater compositions in the basement is then the withdrawal of H₂O from the groundwater and its chemical fixing in zeolite. This desiccation process increases the concentration of the solutes but does not change the pH of water, in accordance with the data from deep groundwater in basement rocks of the Black Forest area. Active ongoing H₂O-consumption by the described desiccation process is supported by the observation of decreasing hydraulic pressure with increasing depth in the earth crust. We present evidence of the continuous operation of H₂O-consuming reactions in crystalline basement rocks from the deep research HDR well in gneisses at Urach (the Urach basement represents a Eastern continuation of the Black Forest basement). The borehole is 4444 m deep today. Originally the hole was drilled to 2500 m and then successively deepened within the last 20 years. We observed that the hydraulic pressure has a continuously dropping potential with increasing depth. At all depth levels of the borehole, the water table never reached stable constant conditions (neglecting earth tides influences and others). The "water-tables" continuously dropped over several years of observation indicating a ceaseless H₂O-consumption at depth. We regard these observations as a strong evidence for active transformation of fresh basement rocks with feldspar and mica into alteration products containing zeolites and clay thereby consuming H₂O from the groundwater in the fracture aquifer.

FMF4 Sulphur Geochemistry and Gases in Geofluids

FMF4 ; TUp05 : PO Field Investigations into the Capability of Gas Bubbles to Transport Particles Upwards Through Saturated Sediments

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In the safety and performance assessment of deep geological radioactive waste repositories, all possible transport pathways of radionuclides to the biosphere must be studied. One possible mechanism is related to the upward migration of a separate gas phase and the possibility that these bubbles may adsorb and subsequently transport particles. If this phenomenon occurs in natural systems it would represent a rapid and effective mechanism for transporting radionuclides away from a repository towards the surface. The present study focused on obtaining field evidence of the transport of microparticles (on the order of <10 microns) adsorbed onto gas bubbles rising through a saturated stratigraphy. This work formed a part of the EC-funded PROGRESS project: "Project of research into gas generation and migration in radioactive waste repository systems", contract F14W-CT96-0024, between May 1996 and April 1999.

The Sasso di Furbara region, located about 50 km north of Rome in the Tolfa-Cerite Volcanic District, was chosen for study because this mining district has active gas manifestations, which may act as a natural analogue. Field investigations included geological, geophysical and soil-gas surveys to define geochemically-active areas; in these locations shallow wells were drilled and filters were floated 4 cm above the water table to trap any particles released from bubbles bursting at the water-air interface. Only the mineralogical results from these filters are described here. A total of 10 wells were drilled to a depth of between 4 to 10 m and three series of filters were placed in the wells for periods ranging from 1 to 6 weeks; one blank was also collected during each sample series. In addition four water samples were filtered and both the aqueous phase and soil-gas particles were analysed. A total of 25 filters (including blanks) during three sampling campaigns were analysed for particles using a Scanning Electron Microscope (SEM); not all wells produced filters for each series due to low water table conditions and other unforeseen events. A significant number of particles were found deposited on the filters floating above the water surface, with a much higher percentage of these particles containing heavy elements than did those filtered from the well water itself. In addition these elements were not found in the large number of surface samples collected from the host rock material, nor were they found in samples taken from the drill bits or from the paint covering the well casing. These results imply that the particles were transported from depth; among the possible mechanisms to explain these results, the adsorption of particles onto rising bubbles appears one of the most probable.

FMF4 ; TUp06 : PO Fluid Inclusion Investigations on Fissure Minerals from NEAT Transects (Gotthard and Löttschberg Base Tunnels) Through the Central Alps: Preliminary Results

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Alpine fissures in NEAT boreholes, shafts and tunnels are generally small hydrothermal systems which formed during prograde and/or retrograde Alpine regional metamorphism. Investigation of fluids, fissure minerals and hydrothermally altered host rocks of the extensional veins is ongoing in order to accomplish the following aims: 1. to understand the evolution of deformation, fluid composition, temperature and pressure during uplift and cooling of the Central Alps 2. to recognize the origin and fluid flow paths of mineralizing fluids 3. to document the mass transport from

the unaltered host rock into the Alpine fissures under continuously changing conditions 4. modelling of fluid-mineral equilibria.

The Alpine fissures sampled are from surface and subsurface locations along the line of the NEAT Gotthard and Löttschberg base tunnels. Microthermometric investigations on fissure quartz yield the following preliminary results: - Higher hydrocarbon-rich and methane-rich fluid inclusions are detected in the exploratory tunnel and boreholes between Fruttigen and Kandersteg (Löttschberg base tunnel). These hydrocarbon dominated fluids were formed and trapped between 150 and 270°C and c. 1 and 2.7 kbars. Fibre, prismatic and skeletal quartz as well as calcite precipitated from these fluids. In the autochthonous cover of the Gasteren Massif hydrocarbon rich fluids were replaced by carbon dioxide bearing water-rich fluids filling Alpine fissures nearly completely with calcite. - Water dominated fluids are common in rare earth element mineral bearing Alpine fissures from the service tunnel at Amsteg (Gotthard base tunnel). They were trapped at retrograde PT-conditions between 350 and 250°C and 3.4 and 2.2 kbars. Late tectonic events allowed carbon dioxide enriched fluids to enter into the water dominated hydrothermal system precipitating siderite in already formed Alpine fissures. Water-rich fluids are also dominant in the service tunnel and vertical shaft at Sedrun. South of Sedrun, water-rich fluids are dominant and sometimes contaminated with late tectonically controlled carbon dioxide advection. - Carbon dioxide dominated fluids are found in Tessin habit quartz from the exploratory tunnel at Piora-Mulde. These fluids were trapped in crystals which formed at 430 ±20°C and 2 to 3 kbars (MULLIS et al., 1994).

Mullis J, Dubessy J, Poty B & O'Neil J, *Geochim. Cosmochim. Acta*, **58**, 2239-2267, (1994).

FMF4 ; TUp07 : PO The Diagenetic Sulfur System in Late Paleozoic Sediments

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The biogeochemistry of marine sediments has been of interest to researchers for a long time. Of prime importance in this respect are biologically controlled processes along a strong redox gradient. In particular, bacterial sulfate reduction appears to be the key process in the anaerobic mineralization of sedimentary organic matter and is considered to be second in overall magnitude to aerobic respiration (e.g., Canfield, 1991). In addition, a whole suite of biologically controlled processes within the sulfur cycle operates in modern marine sediments and results in frequently metastable products, such as thioulfate. Many of these redox processes are associated with distinct and sometimes substantial sulfur isotope effects, which can, thus, yield important information in respect to sulfur diagenesis.

Dependent upon preservation within individual stratigraphic units, the following operationally defined phases have been studied: acid volatile sulfur (AVS), chromium chloride sulfur (CRS) and organic-(kerogen)-bound sulfur (OBS). In particular, pyrite resulting from bacterial sulfate reduction and subsequent reaction of hydrogen sulfide and detrital iron, represents the most stable sulfur phase in marine sediments. This overall process occurs potentially over a wide time window from syndepositional to early diagenetic to late diagenetic, with no quantitative time constraints. The geochemical conditions during pyrite formation, however, can be elucidated through elemental abundances of organic carbon, pyrite sulfur, reactive iron and their respective relationships (e.g., Raiswell et al., 1994; Raiswell and Canfield, 1998). The sulfur isotopic composition, in addition, provide excellent evidence for its biological origin and the relative timing of sulfide formation. Both aspects relate to the distinct fractionation and progressive evolution of the sulfur isotope system. In part, this can be correlated with changes in pyrite morphology.

The clear identification of the diagenetic history of sedimentary sulfur components represents an integral part of our study related to the Paleozoic sulfur cycle, which focusses on the late Silurian to Carboniferous. Due to its relative stability in ancient marine sediments, pyrite is our central target. Its isotopic composition is utilized as our prime proxy signal. In addition, kerogen-bound sulfur is studied when present. Isotope values for these predominantly reduced sulfur species are set in perspective to a

newly developed isotope record for seawater sulfate which is based on the analysis of structurally substituted sulfate in biogenic carbonates.

Canfield, DE, *Amer. J. Sci.*, **291**, 177-188, (1991).
Raiswell R, Canfield DE & Berner RA, *Chem. Geol.*, **111**, 101-110, (1994).
Raiswell R & Canfield DE, *Amer. J. Sci.*, **298**, 219-245, (1998).

FMF4 ; TUp08 : PO Using Stable Sulphur Isotopes as a Method for the Delineation and Examination of Drill Cuttings Piles

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Using stable sulphur isotope ratios (e.g. $\delta^{34}\text{S}$) we have examined the physical and biological processes effecting and the extent of pollution associated with drilled cuttings disposed of at two different rig sites in the North sea.

Drill Cuttings are produced when oil wells are drilled. Barite BaSO_4 with associated $\text{BaAl}_2\text{Si}_2\text{O}_8$ are used as a weighting agent in the mud and contains in many cases heavy metal impurities e.g. Pb, Sr, in the form of sulphates and sulphides e.g. Pb, Fe, Mn, Zn etc. Other metals including As, Cu, Ni, Co, Cr, Cd, Sn, Sb, Bi, Hg, Te are also found. Barites are known to have isotopic ratios for sulphur that are specific to the ore body mineralogy. Drilled cuttings and associated barite rich drilling muds are discharged to the sea bed, following initial cleaning, where they form piles of impoverished sediment. These drilling wastes can contain metals at levels several times levels found in surrounding marine sediments. The Isotopic signature of these deposits can be used to delineate the extent of the contamination. Changes in the stable sulphur isotopes, it can be suggested, may also indicate early diagenesis of these anthropogenic deposits by, general weathering or by formation, derived sulphate reducing bacteria. These sulphate reducers seem to form a symbiotic relationship with methanogenic bacteria in these types of sediments.

The isotopic data from two sampling trips examine the extent in terms of depth profiles and distance from the rig of the cuttings pile and can be utilized as indicators of the presence of elevated levels of specific heavy metals, Ba, Pb, Sr, Zn measured by X-Ray Fluorescence Spectrometry, associated with the cuttings.

The complexities of the sulphur system and the interaction between differing components are discussed and the possibilities of further work involving the use of microcosms to define the processes at work on similar material is discussed.

FMF4 ; TUp09 : PO Sulphur Redox Reactions during Low Grade Metamorphism

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Sulphate evaporite minerals can constitute a significant reservoir of oxidized sulphur in many sediment sequences. Upon burial and heating, sulphate may undergo reduction to elemental sulphur or sulphide via thermochemical sulphate reduction (TSR). This reaction is well-known from organic-rich oilfield systems and we describe analogous reactions from low grade metamorphic rocks and examine their consequences for sulphur mobilization.

FMF4

Sulphur Geochemistry and Gases in Geofluids

Vein deposits containing native sulphur, gypsum, quartz with anhydrite inclusions and rare sphalerite are described from very low grade lacustrine evaporites (alternating dolomite and gypsum) in the Cameros Basin, NE Spain. Fluid inclusion homogenization temperatures and quartz-sulphate-oxygen geothermometry indicate formation at c. 225°C. Fluid inclusions contain elemental sulphur along with a mixture of H₂S, N₂, CO₂ and minor CH₄. These are all likely reactants and products of elemental sulphur generation by TSR and we conclude that a TSR-type reaction was responsible for the genesis of these veins during low-grade metamorphism. These TSR reactions generated water molecules with ¹⁸O-enriched oxygen atoms derived from sulphate molecules and this is reflected in a very high calculated δ¹⁸O of water (+15‰_{SMOW}) in equilibrium with vein sulphate and quartz. Thus TSR-type reactions were sufficient to modify, locally at least, the isotopic composition of metamorphic fluids.

The TSR reactions we observe in this low-grade metamorphic setting differ from those described from most petroleum-related sour gas settings in two ways. Firstly there is no evidence of any secondary carbonate precipitation. Secondly, significant S isotopic fractionations are observed between sulphate (at around +20‰_{CDT}) and reduced products (elemental sulphur is around -11‰_{CDT}). The most likely cause of this isotopic fractionation is increased rates of isotopic equilibration compared to rates of sulphate reduction in the hotter but more organic-poor conditions of low grade metamorphism.

