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., HCFC's, CFC's, perfluorocarbons). For some compounds (CH_2Cl_2, $CHCl_3$ etc.), concentrations are several orders of magnitude greater than present-day atmospheric backgrounds, and above midlatitudional 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 SO_2-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 occurences of hydrogen sulfide (H_2S) 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 H_2S 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 H_2S level have been explored and compared with the reported H_2S abundances. 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/propionic 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 O_2-fugacity follows a trend between the hematite-magnetite and magnetite-pyrite-pyrrhotite buffers. A corresponding H_2-fugacity was also established.

Giggenbach (1980), in his work on gas abundancies and distribution in hydrothermal systems in New Zealand, advocated equilibria between aluminumsilicates 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 H_2S concentrations are buffered by iron sulfide-carbonate assemblages within the reported variation of the $FeCO_3$ component. This behaviour suggests the anhydrite containing reservoirs which may produce high level of H_2S by reactions with hydrocarbons.

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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 $H_2S(HS^-)$ and HCO_3^- (CO_2). 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.

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H₂S in North Sea Oil Fields: Importance of Themochemical Sulphate Reduction in Clastic Petroleum Reservoirs

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H_2S 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 H_2S, 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. H_2S 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, H_2S and the oil-sulphur content are not inversely correlated: H_2S 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 H_2S). There is a positive correlation between the sulphur isotope ratio of oil and H_2S concentration again suggesting that TSR-H_2S 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. H_2S 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. H_2S 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 H_2S has been scrubbed by Fe-minerals producing diagenetically late-stage pyrite cement, common in many North Sea reservoirs.