

ples analyzed so far. While the gas fraction can be depleted in deuterium by about 55 to 70‰ relative to the oil fraction, there is practically no detectable difference in  $\delta D$  values between liquid and wax fractions of a crude oil. It thus appears that the variation in  $\delta D$  values in crude oils in general is not caused by the compositional difference. However, under unusual situations such as "oil" distilled from the Kenai gas, the effect of chemical composition can be important. Evidence also shows that the variation in  $\delta D$  values of crude oils is inherited from the source materials.

There exists correlation between latitude of sampling sites and  $\delta D$  values of crude oils. This indicates that terrestrial organic substance is a major component of source material for most crude oils. The results also seem to support the hypothesis that the lipid fraction is the major biologic source of petroleum. It also can be concluded from the results that the hydrogen isotopic data are useful in correlation between source rocks and reservoirs of petroleum and among crude oils of common origin.

There are no systematic relationships between  $\delta D$  and  $\delta C^{13}$  values, and between  $\delta D$  values and geologic ages of the crude oils analyzed so far.

V 2

THE MODELING OF KINETICS AND TRANSPORT PHENOMENA IN EARLY DIAGENESIS

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The physical chemistry of diagenetic processes in marine sediments must be understood if we are to estimate its role in the overall geochemical cycle of the oceans. The stress in recent research has been away from simple thermodynamic models and towards models that incorporate the kinetic and transport phenomena involved. Much work is still needed in this area. We have developed a model to analyze the general problem of multi-component diffusion in marine processes. The main result links the coefficients for cross diffusion of ions  $i$  and  $j$ ,  $D_{ij}$ , to the self-diffusion coefficients of ions in sea water,  $D_i^0$ , and their concentration  $C_i$ . We contend that this coupling between ionic fluxes can be especially important in estimating the movement of major ions (e.g.  $HCO_3^-$  or  $SO_4^{2-}$ ) between oceans and sediments.

The problem of analyzing observed pore water concentration profiles in a kinetic model is increased when the steady state assumption is not invoked (Lasaga and Holland, 1976). We have simplified our earlier treatment of non-steady state processes, obtaining quantitatively useful rules for calculating response times of the sediment system to time dependent phenomena. The response times are shown to depend on simple but non-obvious relations among the sedimentation rate,  $w$ ; the ion diffusion coefficient,  $D_i$ ; and the kinetic rate constant,  $k$ , for decomposition of organic matter (e.g.  $\tau \sim D_i / w^2$  for certain ranges of values of  $k$ ). With these rules, we can attempt to relate the present-day data to the recent history of the sediments.

Finally a generalization of the current description of biological kinetics is examined.

V 3

HYDROTHERMAL REACTION OF BASALT AND SEA WATER AT MID-OCEANIC RIDGES: A THEORETICAL APPROACH

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The hydrothermal reaction of sea water and mid-oceanic ridge basalt has been numerically modelled under the assumption of partial equilibrium for both closed and open systems over the temperature range 150-330°C at 500 bars and at steam saturation pressures. Computations were performed using a new hybrid program which combines the PATH approach of Helgeson with a modified Newton-Raphson method. The latter permits strict control of accuracy and the capability to change temperature and pressure. The theoretical mass transfer, compositions, and phase assemblages agree well with reported laboratory experiments and observations at the Reykjanes geothermal field for the appropriate conditions of temperature, pressure, and high rock/water ratios. Significant degrees of mass transfer occurred even at low rock/water of 4-20 g basalt kg<sup>-1</sup> water for Mg, S (water to rock) and K, Ca, Fe, Mn, Si (rock to water). Estimates of the mass transfer of major elements between the

oceans and the basaltic crust constrain the rock/water ratios to these low values, indicating that at most 2-8% of the basalt (equivalent to a thickness of 100-400 m) reacts in mid-oceanic ridge hydrothermal systems. Sufficient iron and manganese are mobilized to account for hydrothermal deposits on the sea floor.

V 4

OXIDATION FRONT DURING THE LOW TEMPERATURE SUBMARINE ALTERATION OF MID-ATLANTIC RIDGE BASALTS

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We present part of the results of an integrated geochemical-mineralogical study of the low-temperature processes which affected the uppermost 85 m of sparsely phryic pillow basalts cored at site 396B of IPOD Leg 46. The oceanic crust at this site is about 10-13 MY old. Samples representing several alteration sequences were selected on the basis of megascopic properties such as color, nature and density of fracture and vein fillings, and alteration of olivine phenocrysts. Several low-temperature processes affected the mineralogical and chemical compositions of the basalts which include weathering, deuteric and hydrothermal alterations. The most visible effect of these combined alterations, is related to an oxidation front: the abrupt transition between oxidized (brown) and relatively non-oxidized (gray) altered rocks which occurs within a 2 mm thick zone, suggests a very sharp alteration gradient. The lack of gradation is indicated by a strongly bimodal distribution of the  $Fe^{2+}/Fe^{3+}+Fe^{2+}$  ratio (gray = .3; brown = .6) and of MgO wt. % (gray = 7.5; brown = 4.0) for uniformly colored samples. Variations within each of these two groups exist, especially among the brown rocks. Fissures along which the altering solutions probably circulated are filled symmetrically—from wall to center—with smectites, Fe-Mn hydroxides, phillipsite, and Mg<sub>5</sub>Ca calcite. Brown (more oxidized) basalt adjacent to the secondary mineral veins are characterized by an abundance of the same secondary minerals, and by the absence of fresh olivine. The gray (less oxidized) rocks farther away from the veins often display calcite and/or smectites vug fillings.

V 5

FORMATION CONDITIONS OF IDDINGSITE\*

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The origin of iddingsite is highly controversial because all attempts to synthesize it have failed. Thus, its exact formation conditions remain unknown. Some investigators suggest that iddingsite forms simultaneously with the cooling of the extruded lava, while others believe that iddingsite is a weathering product. In this study, the quantity of iddingsite in several basalt flows of different ages was determined, the quantitative ratios of iddingsite to the other minerals and ions in the examined basalts were established, and a correlation between the quantity of iddingsite and the age of each flow was calculated. Results of this investigation indicate that the formation of iddingsite is highly dependent on the presence of several ions other than iron, and suggest that under the proper geochemical initial conditions iddingsite starts to form with the cooling of the extruded lava and continues to form as a result of weathering. These findings can explain the failure of previous attempts to synthesize iddingsite by using a variety of temperature and pressure conditions but using only pure iron-bearing minerals as the source.

\* This study was conducted while at New Mexico Institute of Mining and Technology.

V 6

OXYGEN ISOTOPIC EVIDENCE FOR METEORIC-HYDROTHERMAL ALTERATION OF THE JABAL AT TIRF IGNEOUS COMPLEX, SAUDI ARABIA.

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The  $^{18}O/^{16}O$  ratios of rocks and minerals from the 22 m.y. old Jabal at Tif complex are very low and highly variable. Layered gabbro:  $\delta^{18}O$  plagioclase (An<sub>62</sub>-An<sub>72</sub>) = -1.7 to +5.2,  $\delta^{18}O$  clinopyroxene = +1.3 to +5.0,  $\delta^{18}O$  plag-px = -4.6 to +0.1. Granophyres:  $\delta^{18}O$  whole rock = -0.5 to +1.8,  $\delta^{18}O$  quartz = +0.2 to +3.9. Diabase dike swarm:  $\delta^{18}O$  whole rock = -1.4 to +3.7. The negative  $\delta^{18}O$  plag-px values indicate that the entire 1800 meter-thick layered gabbro has been depleted in  $^{18}O$  subsequent to crystallization, with the most extreme depletion occurring in the plagioclase from the upper 600 m and at the base. Comparing nearby samples within the stratigraphic sequence, slightly higher Na contents tend to occur in the more  $^{18}O$ -depleted feldspars, but the extreme  $^{18}O$ -depletions are not accompanied by any major chemical changes in the plagioclase. These data imply that large volumes of heated meteoric ground waters circulated through this complex, which represents a spreading center associated with the opening of the Red Sea. The Jabal at Tif complex has many features in common with ophiolite complexes, the major differences being the presence of an overlying section of non-marine sediments and the lack of pillow lavas, the much lower  $\delta^{18}O$  values, and the fact that the granophyres and silicic dike rocks are strongly potassic rather than sodic. We propose that these differences are basically because low- $^{18}O$  meteoric ground waters, rather than NaCl-rich ocean waters, were involved in the hydrothermal convective system associated with the emplacement of this complex. The features in this complex are similar to those observed in the East Greenland dike swarm in the vicinity of the Skaergaard intrusion.

V 7

ZEOLITE FACIES METAMORPHISM OF BASALTIC ROCKS FROM THE EAST TAIWAN OPHIOLITE

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The fragmented East Taiwan Ophiolite exists as allochthonous blocks in the Pleistocene Lichi Mélange. It consists successively upward of (1) angular polymict breccia of gabbro, peridotite and related rocks, (2) a thin layer of red shale, and (3) an extrusive tholeiite sequence from minor massive flows to brecciated and dominant close-packed pillows. The basaltic rocks are extremely low in K<sub>2</sub>O and TiO<sub>2</sub> and are high in CaO and MgO/FeO\*; they are mineralogically and chemically similar to oceanic basalts. The basaltic rocks have been subjected to "ocean-floor" zeolite facies metamorphism. Depending on the bulk composition and modes of occurrence, various mineral assemblages occur: thomsonite + analcime + chabazite; pumpellyite + chlorite + laumontite in veins of the pillow cores; and pumpellyite + chlorite + K-feldspar; pumpellyite + laumontite + thomsonite, and prehnite (about 3 wt% Fe<sub>2</sub>O<sub>3</sub>) + hematite in veins of the pillow matrices. Plagioclase phenocrysts were replaced by albite + pumpellyite + Ca-zeolites, pumpellyite + K-feldspar, analcime + chabazite + thomsonite, or by K-feldspar alone, the olivine phenocrysts by brown chlorite + serpentine + pumpellyite, but the pyroxenes are well preserved. Except for local palagonitization along fractures and rims, the pillowed glassy rims are perfectly fresh. Pumpellyites characteristically contain up to 25 wt% total Fe as FeO, higher than most reported pumpellyite (except julguldite). Calculation of their structural formulas indicates that they may contain iron dominantly in the ferric state. Substitution of Fe<sup>3+</sup> for Al in this phase evidently enlarges the pumpellyite P-T stability field relative to the zeolite facies assemblages under oxidizing conditions. The basaltic rocks of the East Taiwan Ophiolite were hydrothermally metamorphosed at T = 150-250°C and depths of 0.6 to 1.6 km.