Selected Authors' Abstracts

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INTERACTION BETWEEN SEA WATER AND OCEANIC LAYER TWO AS A FUNCTION OF TIME AND DEPTH

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Circulating sea water through oceanic basalts may be an important mechanism in the extraction, concentration and re-deposition of economically important metals on the ocean floor. Different reports of the action of halmyrolysis have, in the past, given controversial results without any clear geochemical trends emerging. Data on the geochemical variations of basalts from four "field" investigations, and from two sets of laboratory experiments are presented and discussed. The "field" investigations show chemical changes (1) with the time from zero to 16 m.y. on basalts from the M.A.R. at 45°N, showing the different degrees of alteration with age (2) with depth through large pillows from the M.A.R. at 36°N and (3) with depth through thick submarine flows drilled from Bermuda during Deep Drill-1972, and (4) with depth down the deep holes drilled during Deep Drill-1974 by the Glomar Challenger on D.S.D.P. Leg 37. Laboratory experiments included (1) interaction of excess sea water with a basalt column having an internal 100°C thermal gradient (2) interaction of circulating excess sea water under pressure through various interconnected basalt columns held with temperature differences between columns of up to 300°C. The latter represents a close laboratory simulation of ocean floor conditions.

THE EFFECT OF COBALT ION ON NUCLEATION OF CALCIUM CARBONATE IN MODEL SEAWATER SYSTEMS

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Solutions containing NaCl and $CaCl_2$ and having the ionic strength and calcium content of seawater (35 ‰ salinity) were spiked with known amounts of $CoCl_2$. Calcium carbonate was precipitated by the addition of 0.7 ml of 1 *M* Na_2CO_3. All experimental runs were made at 25°C. All precipitates were examined by *x*-ray diffraction. At low concentrations of cobalt ($1\text{x}10^{-4}M$) calcite and vaterite formed. As the concentration increases ($1\text{x}10^{-3}M$) calcite, vaterite and aragonite formed. At concentrations above $0.3\text{x}10^{-2}M$ pure aragonite or aragonite with traces of calcite were the only crystalline precipitates formed. All precipitates contained an amorphous, violet phase, assumed to be basic cobaltous carbonate ($2CoCO_3 \cdot Co(OH)_2 \cdot H_2O$).

The results indicate that cobalt, like magnesium, may cause the precipitation of aragonite rather than calcite in aqueous solutions. The effect of cobalt in solution may be similar to that suggested for magnesium, *i.e.* adsorption and crystal poisoning of calcite by a hydrated ion.

THE ROLE OF WATER FUGACITY AND OXYGEN FUGACITY DURING ANATEXIS IN THE MANTLE

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Experimental investigations of melting and other phase relationships of peridotite, basalt, and andesite under a range of controlled values of water fugacity (f_{H_2O}) and oxygen fugacity (f_{O_2}) reveal that these parameters are as important as composition, pressure, and temperature (degree of melting) in determining the nature of the anatectic liquids. Experimentally we used two methods to control f_{H_2O}: (1) reduced the amount of H_2O in the charge so that it was all dissolved in hydrous minerals or in a silicate melt, and (2) added a second volatile component (CO_2) to the aqueous vapor phase. The second method was used in most runs because the vapor phase promotes equilibration and an aqueous vapor is necessary to control f_{O_2} using solid-phase buffers and the double-capsule techniques.

To assess the role of bulk composition on the temperatures of the beginning of melting, four peridotites (lherzolites) and a websterite were investigated from about 750° to 1250°C to pressures of 30 kbars under conditions where the mole fraction of H_2O in the vapor phase ($X_{H_2O}^{V}$) was about 1 and with f_{O_2} ranging from those of Magnetite-Hematite (MH) to Iron-Wustite (IW). Under similar conditions of f_{O_2} and f_{H_2O}, the temperature differences between the solidi of the peridotites are as great as 200°C. The major effect of increasing f_{O_2} through the range studied is to strongly fractionate Fe^{3+} into the liquid relative to the crystalline phases, significantly decreasing the

Mg/(Mg + Σ Fe) of the liquid coexisting with forsterite-rich olivine (Fo_{92}). Low values of f_{O_2} also lower the f_{H_2O} because of the concomitantly large f_{H_2}.

The effect of lowering f_{H_2O} by adding various mole fractions of CO_2 to the vapor is primarily to reduce the proportion of SiO_2 in the anatectic liquid. Liquids as much as 200°C above the solidi are quartz normative ("andesitic" for $X^{V}_{H_2O} \geqslant 0.6$, ranging to nepheline normative ("nephelinitic" or "melilititic") at $X^{V}_{H_2O} \sim 0.25$. This change primarily reflects the effect of f_{H_2O} on the melting behaviour of the *orthopyroxene*, being $Opx + V \rightleftarrows L$ at $X^{V}_{H_2O} \geqslant 0.6$ and $Opx + V \rightleftarrows Ol + L$ at lower values. Supportive results were obtained in synthetic, relatively simple systems in which f_{H_2O} was controlled by the first method.

In hydrous basaltic systems at depths less than about 100-75 km, *amphiboles* control the compositions of liquids derived by anatexis or fractional crystallization. Stability of the amphiboles is in turn dictated by both f_{H_2O} and f_{O_2}. For example, lowering f_{O_2} decreased the pressures at which amphiboles break down to garnet-bearing assemblages. Separation of these SiO_2-poor pargasitic or tschermakitic hornblendes ($SiO_2 \sim 43\%$) either as early crystallizing phases near temperatures of the liquidus or as residua during anatexis produces quartz-normative "andesitic" liquids.

GEOCHEMICAL STUDIES OF RED SEA CORES

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Geochemical and isotope studies show that the non-carbonate fractions of sediment samples from piston cores taken in the median valley of the Red Sea can be regarded as mechanical mixtures of two components. These components are 1) weathering products of old sialic rocks derived from the surrounding land masses of Africa and the Arabian Peninsula; and 2) volcanic dust and weathering products of young volcanic rocks which are predominantly basaltic in composition. The strontium concentrations and isotopic ratios of the non-carbonate samples were determined, and these data were shown to fit a hyperbolic curve that results from the mixing of the two components. By assuming reasonable values for the 87Sr/86Sr ratios, the strontium concentrations of the basaltic and sialic components were determined by solving the mixing equations derived from the data. Using these compositions for the end members, the per cent concentration of the basaltic component in each sample was calculated from the relevant mixing equations. The systematic variation in the concentration of the basaltic component with depth in the cores was used to define stratigraphic layers. These stratigraphies define sialic-rich and basaltic-rich layers which are consistent with mineralogical and chemical differences as determined by conventional methods. This new technique not only provides an easy method of developing correlatable stratigraphies but also conveys precise information concerning the provenance of the sediment in the depositional basin.

NEW DATA ON SOME MINERALS IN THE Pd-As-Sb-Bi SYSTEM

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Recent mineralogical studies of samples from diverse localities have indicated the presence of several new minerals as well as contributed to a further understanding of previously described species. New minerals found are $Pd_8(As,Sb)_3$, Pd_8Sb_3, Pd_5As_2, and $Pd_2(As,Bi)$. The $Pd_8(As,Sb)_3$ mineral is hexagonal and equivalent to the $Pd_{2.65}As$ phase synthesized by Saini *et al.* (1964). The Sb-free end-member has a = 7.399(4), c = 10.311(15)Å and the most Sb-rich grain has a = 7.39(1), c = 10.30(1)Å. The second occurrence, world-wide, of palladoarsenide (Pd_2As) is also reported as are new analytical data for arsenopalladinite and mertieite II. Results of preliminary experiments in the Pd-As-Sb and Pd-As-Bi systems are discussed in conjunction with the minerals found in nature and tentative conclusions regarding the stoichiometry of these minerals will be presented.

COMPOSITIONAL VARIABILITY IN WELLSITE

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Phillipsite $(Na,K)Ca_2Al_5Si_{11}O_{32}\cdot 12H_2O$ and harmotome $(K,Na)Ba_2Al_5Si_{11}O_{32}\cdot 12H_2O$ are well-established minerals with chemical variability and crystal structures known in detail. The Ba content of phillipsites only exceptionally exceeds 0.10, and the Ba content of harmotomes seldom drops below 1.80 (atoms per 32 O of the above formulas). The rare intermediate compositions showing Ba contents in the range 0.20-1.50, mostly described as wellsites, are known to a much lesser degree. Electron microprobe analyses of wellsites from three localities show very wide variations in the contents of most oxides within individual multiple-penetration twins, *e.g.*, SiO_2 39.3-50.6, Al_2O_3 15.5-22.6 CaO 2.7-7.5, K_2O 1.5-4.8, Na_2O 0-0.6, BaO 2.1-19.5 wt. % (Věžná, Czechoslovakia). Microprobe analyses run along cross-sections of multiple-penetration twins from two localities reveal a distinct zoning. In cores, phillipsitic patches are surrounded by material of variable but generally intermediate composition; marginal portions are close to pure harmotome. Despite this highly variable cationic content and Si/Al ratios, the wellsites produce good *x*-ray powder diffraction patterns, and the refined monoclinic cell dimensions show standard deviations within 0.003-0.007Å and 2-3′. The chemical variability, covering practically the full phillipsite-harmotome range, makes the status of wellsite as a mineral species rather questionable. On the other hand, the occurrences of wellsites seem to be typical of certain parageneses.

SOME SIGNIFICANT CHEMICAL AND BIOLOGICAL PROCESSES IN GEOCHEMICAL STUDIES

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The studies of some chemical and biological processes will help to gain further insights and to create new approaches to many basic geochemical research areas in the aquatic system. Complex equilibrium and solubility-product constants can be used to interpret solubilization and precipitation of minerals. Organic geochemistry has long been studied at the atomic level. Separation of naturally occurring organics and studies on their interactions with metals open up another horizon of molecular geochemistry. Biological formation of organo-metal compounds results in redistribution of certain elements between sediment, water and gaseous phases. Studies of the speciation of elements in the aquatic system contribute to further understanding of the thermodynamics of the system. Modern instrumental techniques for these studies will also be discussed.

SEDIMENTARY, GEOCHEMICAL AND FOSSIL DIATOM ANALYSIS OF SEDIMENT CORES FROM LAKE MACATAWA: AN ASSESSMENT OF MAN'S IMPACT

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Sedimentary, geochemical and fossil diatom analysis of piston cores from Lake Macatawa, Michigan were conducted, and the recent history of that water body has been found to be well-documented within the sediment column. Our findings have enabled us to assess man's impact upon that aquatic environment for which there is an absence of scientific background information.

Enrichment of Cu, Cr and Zn toward the tops of cores coincides with a substantial increase in total phosphorus and with low-diversity, eutrophic diatom assemblages. These changes attest to the deterioration of the Lake Macatawa environment due to industrialization and urban development.

Sedimentary changes within cores reflect a major increase in sedimentation during modern times, and is attributed to increased agricultural activity within the drainage basin and to natural causes. Sedimentation rates in excess of 3cm/yr for the past 100 years were derived from trace metal horizons in cores.

Recent efforts to improve the quality of Lake Macatawa have been successful. Significant reductions in heavy-metal concentrations in the tops of cores taken near industrial sites are coincident with changes in diatom assemblages, and reflect a decrease in eutrophication of the lake.

A NUMERICAL APPROACH TOWARD THE CLASSIFICATION OF COMPLEX, ORTHORHOMBIC, RARE-EARTH AB_2O_6-TYPE Nb-Ta-Ti OXIDES

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Since their initial description in the early 1800's these Nb-Ta-Ti oxides have been a "mineralogical headache." Due to complex compositions, their metamict state and pervasive alteration, as well as errors of previous workers, the nomenclature of this mineral group is often inconsistent and ambiguous.

To test the consistency of the nomenclature of previous workers and to develop a consistent chemical nomenclature, five groups — euxenite, polycrase, priorite, blomstrandine and aeschynite — were subjected to stepwise discriminant analysis. The literature data set contained 91 cases. Each case consisted of a maximum of 58 chemical, physical, optical and structural variables for which a symmetric correlation matrix was calculated. Output for the discriminant analysis was plotted in the plane of the two principal canonical variables using various combinations of seven chemical variables: TiO_2, Nb_2O_5, Ta_2O_5, ΣCe_2O_3, ΣY_2O_3, $\Sigma U_3O_8 + UO_2 + UO_3$, ThO_2.

The results of the multivariant analysis and a program of classification improvement (Demirmen 1969) using the seven chemical variables indicate at least a three-fold chemical classification — aeschynite, euxenite and polycrase. These groups may be distinguished on the basis of only three chemical variables:

	euxenite	polycrase	aeschynite
TiO_2	22.28±3.06	32.47±4.01	21.05±5.09
Nb_2O_5	26.91±5.22	18.71±5.04	30.57±9.25
ΣCe_2O_3	2.13±1.28	2.47±1.17	20.95±6.63

MINERAL RARE EARTH ELEMENT DISTRIBUTION IN EUDIALYTE-BEARING ALKALINE ROCK COMPLEXES

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The rare earth element (REE) compositions of coexisting eudialytes, feldspars and, for some samples pyroxenes, from various alkaline complexes have been determined by thin film *x*-ray fluorescence techniques.

Chandrite normalized REE patterns of eudialytes fall into three broad categories: (1) negative Eu anomaly, no light REE enrichment, slight depletion in heavy REE (Seal Lake, Labrador; Magnet Cove, Ark.); (2) negative Eu anomaly, slight enrichment in both light and heavy REE (Norra Karr, Sweden; Kipawa Lake, P.Q.; Ilimaussaq, Greenland) and (3) no Eu anomaly, moderate enrichment in light REE and slight enrichment in heavy REE (Khibiny, USSR).

Coexisting feldspars show little or no fractionation of REE compared to the eudialytes and no preferential enrichment in Eu.

The REE distribution of all samples show evidence of rare earth complexing, of various types which are possibly related to major element geochemical features such as peralkalinity. Eu anomalies are similar for both feldspars and coexisting eudialytes indicating that feldspars are not preferentially incorporating Eu^{+2} from the magma at this stage of differentiation.

THE ROLES OF WATER AND CARBON DIOXIDE IN THE UPPER MANTLE

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Experimental studies have defined a specific model for the existence of the lithosphere and low-velocity zone in the upper mantle in terms of the limited high-pressure stability of a pargasitic amphibole and a region of incipient melting (LVZ) at depths >85-95 km. This model is applicable to a mantle of pyrolite composition with $\lesssim$0.4% H_2O. In regions of higher water content, the lithosphere is thinner (~60 km) and the degree of partial melting in the underlying zone is greater — these conditions probably apply beneath island arcs. Water-saturated melting of pyrolite produces alkali-rich, probably shoshonitic, magmas for very low degrees ($\lesssim$5%) of melting and shallow (30 km) depths of magma segregation. Basaltic andesite to alkali-rich quartz tholeiite result from moderate degrees (15-30%) of partial melting and quartz and olivine-poor tholeiite for high degrees of partial melting at 30-60 km depth. Andesites, dacites or rhyodacites are not produced by partial melting of peridotite at depths $\gtrsim$30 km. Melting of pyrolite containing $\lesssim$0.4% H_2O produces magmas ranging from olivine nephelinite to olivine tholeiite and tholeiitic picrite. Extremely undersaturated magmas such as olivine melilitite require the presence of CO_2 in the source region and, at their depth of origin, contain important dissolved CO_2. The high solubility of CO_2 in olivine melilitite magmas is genetically very important in relation to kimberlite and carbonatite genesis.

TUNGSTEN IN IRON FORMATIONS

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Epithermal neutron activation analysis was used to determine W concentrations in Precambrian iron formations. Analysis by the non-destructive method was successful, with counting errors averaging less than 15%. Iron-formation samples were obtained from Kirkland Lake, Lake Temagami, N.W. Ontario, the Melville Peninsula and Yellowknife, N.W.T. 51 iron formations (oxide, carbonate and sulfide facies), 7 individual oxide facies bands and 7 magnetite and hematite separates were analyzed. Most W values for iron formations range from 0.1-1.0 ppm, with some falling in the 1-14 ppm range, and with one high value of 51 ppm. In 3 distinctly banded oxide facies samples from Temagami and Kirkland Lake, W concentrates in certain bands, the order of preference being hematite > jasper > magnetite > grey chert. Enrichment in W occurs in carbonate facies of iron formation, especially fuchsite schists, relative to oxide facies.

PETROLOGIC SIGNIFICANCE OF REVERSIBLE REACTIONS BETWEEN PYRITE AND PYRRHOTITE IN SO_2

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Differential thermal analyses of iron sulfides in inert atmospheres containing varying amounts of SO_2 indicate temperature dependent reversible reactions between pyrite and pyrrhotite in the range from 350° to 520°C. Hexagonal pyrrhotite and sulfur dioxide interreact above 350° to form pyrite and magnetic, according to the reaction:

$$(1)\ 8FeS + 2SO_2 \xrightarrow{350°C} 5FeS_2 + Fe_3O_4$$

Pyrite decomposes to pyrrhotite and sulfur above 520°C in the same atmosphere, according to the reaction:

$$(2)\ FeS_2 \overset{520°C}{\rightleftharpoons} FeS + S$$

Monoclinic pyrrhotite first inverts endothermically to the hexagonal polymorph near 320°C, and then reacts exothermically near 350°C to a mixture of pyrite and magnetite by combining with sulfur and oxygen from the SO_2 molecule.

The sulfurization of hexagonal pyrrhotite to pyrite has been investigated kinetically by D.T.A. and confirmed by *x*-ray diffraction and wet chemical analyses.

The thermodynamics of this reaction merit both geologic and metallurgical considerations.

TUNGSTEN AND SOME OTHER TRACE ELEMENTS IN BASALTS AND ANDESITES

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Over 100 rocks, mostly basalts and some andesites, were analyzed for W (NAA) and some other trace elements (XRF) (Rb,Sr,Y,Zr,Nb . . .). The samples which represent a very wide range of rocks from oceanic (islands and floor), island-arc and continental areas, contain W abundances from <0.01 ppm to >2.5 ppm. Differences for both tholeiites and alkali basalts exist between the various regions, though not always so pronounced as for other elements, whereas values for island-arc basalts and andesites are well below suggested world values. The correlation between Si and W (Vinogradov *et al.* 1958) though very obvious within a single differentiation sequence, is much less so on a broader scale of sampling. Factor analysis (and other correlation methods) show a more complex behaviour of W, involving as well the alkalis and it also places W among the incompatible elements. Factor analysis proved to be more useful for correlating W with other trace elements and/or major oxides for oceanic and island-arc rocks than for continental ones.

THE METAL ADSORPTION CHEMISTRY OF BUSERITE

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Heavy-metal enrichment of Mn-rich sediments and Mn nodules relative to silica-rich sediments is a well-known geochemical phenomenon. The ubiquity of occurrence of such deposits suggests that they may act as a significant sink for metals. Surface adsorption has been hypothesized as the mechanism yielding this association. A study of the metal adsorption characteristics of a defined Mn mineral species (buserite) was carried out. For any given pH (range 2-7), metal adsorption proceeded Ca $<$ Zn $<$ Cu. Positive metal adsorption was recorded at values approaching pH (ZPC). Data did not agree with a simple 1:1 (Cu:H) exchange model of adsorption; hypothesis of some degree of 1:2 surface exchange and/or specific adsorption may be used to explain this discrepancy.

NEW DATA ON STANNITE AND RELATED SULPHIDE MINERALS

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Studies of stannite, $Cu_2(Fe,Zn)SnS_4$ and kesterite, $Cu_2(Zn,Fe)SnS_4$ from a number of world-wide localities have served to clarify the relationship between the two species and to eliminate some superfluous mineral species and variants. The lattice parameters of stannite and kesterite, both of which are tetragonal, are $a = 5.448$, $c = 10.741$Å and $a = 5.423$, $c = 10.857$Å respectively. The parameters do not vary measurably as a function of composition.

Specimens identical or closely related to type material were obtained for "zincian stannite" (Berry & Thompson 1962), "ferrian kesterite" (Petruk 1973), "unknown mineral" (Petruk 1973), and "isostannite" (Claringbull & Hey 1955). These proved to be as follows:

"zincian stannite" = kesterite
"ferrian kesterite" = kesterite
"unknown mineral" = kesterite + stannoidite ($Cu_8Fe_2ZnSn_2S_{12}$)
"isostannite" = kesterite

MINERALOGICAL ASPECTS OF ENVIRONMENTAL PROBLEMS

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Fundamental mineralogical-petrographic information is required in order to understand environmental problems, as well as to alleviate the problem. This information can also be used for economic gain. Mineralogy of amphiboles is prerequisite to understand the ultimate fate of asbestiform cummingtonite in Lake Superior. Energy dispersive analysis using a transmission electron microscope shows compositional variation of cummingtonite from Fe_3 - to $Fe_{5.4}$ — confirming early studies of Bonnichsen (1969). Composition is important in defining the acicular nature, surface charge and coagulation character of cummingtonite. Acid nonproductive lakes are common in non-calcareous areas adjacent to smelters. The mineralogical nature of unconsolidated sediments is the most important factor in predicting lakes that will be affected in the Canadian Shield. Bauxite wastes pose an environmental problem, yet these wastes specifically adsorb phosphate in sewage outfall. Similarly, tailings with large surface area should be studied for their potential use as adsorbers of contaminants. Al/Si ratios and the isoelectric point of minerals present guidelines for further study.

A PETROGENETIC MODEL FOR THE ASSOCIATION HYPERSOLVUS GRANITE-SUBSOLVUS GRANITE

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Suites emplaced in environments of extensional tectonics are bimodal, characterized by the associations gabbro-granite or alkali gabbro-syenite (or volcanic equivalents). The felsic differentiate is commonly calcium-poor and has hypersolvus mineralogy, *i.e.*, the two alkali feldspars form by exsolution of one primary disordered feldspar. This textural evidence and the common association with rhyolites and granophyres in specific complexes examined in western Quebec, southern New Brunswick, Maine, Massachusetts and Corsica suggest that crystallization occurred at shallow levels, from melts relatively poor in dissolved water. These studies also document the late appearance of a subsolvus granite in which the two feldspars form discrete grains, indicative of higher $P(H_2O)$. It is proposed that a late influx of water, largely of meteoric origin, interacted with the hypersolvus granite once crystallized, inducing local near-complete fusion and remobilization of the early granite. The influx of water is reflected in deuteric changes in the hypersolvus granite: alteration of mafic minerals, deposition of albite, replacement of pre-existing feldspars by alkali exchange, and local increase in degree of order of K-feldspar. The influence of surrounding supracrustal rocks is expressed by selective contaminations in elements carried by the convecting fluid phase, not by anatexis of sialic crust.

GEOLOGIC CONSTRAINTS ON MODELS FOR WET MELTING OF CALC-ALKALINE MAGMAS

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Speculation on the mechanisms responsible for generation of andesitic magmas in orogenic systems eventually reaches an impasse where a choice between conflicting models is only a matter of personal preference, because one can find too little tangible evidence by which the models can be tested. The present need is for fewer models and more geologic criteria that can be related to processes operating at depth.

Many of the popular rules of thumb on which current reasoning is based are open to serious question, and recent studies of the volcanic provinces of the Circum-Pacific region have shown that some commonly accepted concepts may be false. For example, even though andesite may be important in certain times or places, it is not necessarily the principal rock type of these systems. In most belts the relative volumes of basalt, andesite, dacite and rhyolite follow a steady decline with increasing SiO_2. Contrary to widely held belief, volcanic belts that cross from one type of basement to another may show important compositional variations, especially in the relative volumes of rock types and in trace element abundances. Changes transverse to the axes are far from regular. Although the average composition of lavas behind a volcanic front tends to be more alkaline and potassic, the variation is commonly unsystematic and may only be an apparent feature resulting from the distribution of exposures of rock of different ages. The axes of volcanism migrate laterally with time, but some move seaward, some landward and others rotate clockwise or counterclockwise with respect to older axes.

Perhaps the most remarkable aspect of orogenic volcanism is its strongly episodic nature. Cenozoic activity has been marked by brief periods of intensive volcanism, often in unison over wide areas of the globe. These same volcanic events are accompanied by structural uplift and depression along linear belts. Water must play an important role in these events, but the mechanism is poorly understood.

MIASKITIC CORONITES FROM THE BENTLEY-SIDDON LAKES AREA, NEAR BANCROFT, ONTARIO

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Synantetic coronas between nepheline and aegirine-augite occur in non-deformed statically metamorphosed ijolite, lying in a polydeformational and polymetamorphic Grenville terrane. A rigid metagabbro unit envelopes the ijolite and its presence renders tectonic *S*-surfaces nonpenetrative in the area. Textural observations indicate that coronas began forming at the end of a first period of deformation, after the emplacement of the ijolite, and continued developing during and after a second period of deformation. The complex coronas, from aegirine-augite outwards, consist of a grossular-andradite-sphene layer, followed by an equigranular ferrohastingsite- oligoclase layer, and a scapolite layer in contact with nepheline. The bounding primary minerals also show metamorphic transformation. Aegirine-augite is riddled with exsolved blebs of sphene which form nuclei for growth of garnet. Rarely, relict titanaugite can be observed in aegirine-augite grains in areas where sphene has not been exsolved. The least-metamorposed nepheline contains numerous microscopic clinopyroxene needles and has a composition in the range $Ne_{88}Ks_{12}$ to $Ne_{82}Ks_{18}$. More extensive metamorphism clears the nepheline of clinopyroxene and its composition tends towards the Morozewicz-Buerger convergence field.

The transformations involved are, in sequence, the exsolution of sphene from titanaugite to form augite, and the equilibration of nepheline solid solution releasing Ne, Qz, and An components. A part of the Ne component combines with augite to form grossular-andradite and aegirine while a combination of Ne, Qz, and An components form albite-oligoclase, which is scapolitized by the clearing of liquid brine inclusions to the margin of nepheline. Aegirine-augite subsequently breaks down to ferrohastingsite and oligoclase.

SAMUELSONITE, $(Ba,Hole)(Ca,Hole)_2(Fe^{2+},Mn^{2+},Na)_4Ca_8Al_2(OH)_2(PO_4)_{10}$, A FRAGMENTED APATITE STRUCTURE, AND SOME NOVEL INSIGHTS IN THE APATITE STRUCTURE TYPE

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Samuelsonite, $(Ba,Hole)(Ca,Hole)_2(Fe^{2+},Mn^{2+},Na)_4Ca_8Al_2(OH)_2[PO_4]_{10}$, *a* 18.495Å, *b* 6.805Å, *c* 14.000Å, β 112.75°, space group $C2/m$, $Z = 2$, is a new species found with whitlockite and hydroxylapatite at the Palermo No. 1 pegmatite, N. Groton, New Hampshire. $R = 0.084$ for 2571 independent reflections.

Its extraordinary structure is based on apatite fragments consisting of the Ca atoms at $(1/3\ 2/3\ z,\ 1/3\ 2/3\ 1/2 - z;\ 2/3\ 1/3\ \bar{z},\ 2/3\ 1/3\ 1/2 + z)$ and the ten circumjacent PO_4 tetrahedra. Direct comparison between the apatite (down *c*) and samuelsonite (down *b*) structures reveals that the geometrical differences are very slight and that the $[Ca_4(PO_4)_{10}]$ double-column is preserved in every detail. In samuelsonite, it is surrounded by a barrier of $Al_2(OH)_2(Op)_8$ octahedral corner-sharing chains and $(Fe,Mn)_2(Op)_8$ octahedral edge-sharing chains which are oriented parallel to the *b*-axis. In many respects, samuelsonite is a hybrid structure, transitional to both apatite and childrenite-eosphorite structure types.

Samuelsonite opens up possibilities for other exotic apatite-like structures, one of which may have the composition $BaCa_5Al_3(OH)_3[PO_4]_6$ and *a* 15.0Å, *c* 6.8Å, $P6_3/m$, $Z = 2$ as cell criteria. Morphologically, it could easily be confounded with apatite.

DIAGENETIC PHOSPHATE MINERALS AND THE ENVIRONMENTAL CONSEQUENCES OF THEIR FORMATION

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Low-temperature phosphate minerals generally have very low solubilities and their formation is considered to be the buffer mechanism regulating (a) the levels of inorganic phosphorus in many natural waters and (b) the availability of phosphorus in soils. Models depicting the response of iron and manganese phosphates to changes in the chemical conditions of aquatic ecosystems are discussed. The consequences and end-products of phosphate interaction with clay minerals are considered; palmerites and leucophosphites are intermediary phases which may be the major phosphorylating minerals (rather than apatite or struvite) in the prebiotic synthesis of nucleic acids. The reaction of phosphate ions with base-metal pollutants to form insoluble compounds is believed to play a major role in regulating both the loading rates and the concentrations of these metals in some natural water systems.

THE AUTOMATIC EVALUATION OF *X*-RAY POWDER DIFFRACTION PATTERNS AND THE CONSTRUCTION OF DETERMINATIVE CURVES FOR MINERAL COMPOSITIONS

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By coupling an X-Y recording microdensitometer with computer data reduction, a quantitative method of analysis of *x*-ray powder diffraction films has been devised.

Peaks are identified automatically and their positions are refined on the peaks from an internal standard. The relative intensities of peaks are also determined.

The data thus obtained permit the lattice geometry to be defined with high precision. Parameters sensitive to changes in chemical composition of a mineral can be identified and used to construct determinative curves. Such curves relate axial lengths and ratios, cell volume, cell angles and intensities, as well as individual *d*-spacings to mineral composition.

This is illustrated by application to the olivine solid-solution series using films from Debye-Scherrer, Gandolfi and Guinier cameras.

MOBILIZATION IN A MIGMATITE FROM THE GRENVILLE PROVINCE, QUEBEC

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Petrological study of a migmatite outcrop in layered hornblende and biotite gneisses from the Grenville province, Quebec, indicates that the main mobilization of granitic material took place in situ between 700°C and 750°C at an estimated total pressure of about 5 kb. Textures resulting from the reactions

5 diopside + 3 CO_2 + H_2O → tremolite + 3 cal-

cite + 2 quartz (1)
3 hornblende + 5 K-feldspar + $6CO_2$ + $2H_2O$
→ 5 biotite + 6 calcite + 24 quartz (2)
anorthite + K-feldspar + CO_2 + H_2O
→ muscovite + calcite + 2 quartz (3)

are visible in the neosomes and took place with falling metamorphic temperatures after mobilization. During prograde metamorphism, reactions (1) and (2) apparently operated in reverse in the "proto-neosomes" where calcite facilitated the production of water and more K-feldspar below granite solidus temperatures.

Petrological relationships between adjacent paleosomes and neosomes can be explained by anatexis beginning in the "proto-neosomes" where insufficient water was available to saturate the melt. With increase in temperature, water was drawn into the neosome melting sites, whereas no melting occurred in tthe paleosomes despite their containing feldspars identical in composition to those involved in production of melt nearby. The survival, throughout the mobilization process, of fresh biotite in the paleosomes imposes an upper limit to the temperature reached.

AN EXPERIMENTAL STUDY OF PHLOGOPITE SOLID SOLUTIONS IN THE SYSTEM K_2O-MgO-Al_2O_3-SiO_2-H_2O. SOLUBILITY OF TITANIUM IN PHLOGOPITE SOLID SOLUTIONS

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The composition of phlogopite can be expressed by the general formula: $K_2(Mg_{6-x-y}Al_x\square_y)(Si_{6-x+2y}Al_{2+x-2y})O_{20}(OH)_4$, where □ represents an octahedral vacancy. The maximum values of x and y depend strongly on temperature. At 600°C, 1 kbar, the compositional range is maximum. The most aluminous phlogopite obtained in these conditons has $x = 1.625$ and $y = 0.35$. At 800°C, 1 kbar, the compositional range decreases; the most aluminous phlogopite has $x = 0.75$, $y = 0.25$. At 1000°C, 1 kbar, only phlogopite having $x{=}y{=}0$ is stable. Important variations have been observed in cell parameters and infrared absorption spectra of O-H bonds of micas reflecting these variations in composition. The incorporation of Ti^{4+} in phlogopite follows the substitutional model $2Si^{iv}, Mg^{vi} \rightleftharpoons 2Al^{iv}, Ti^{vi}$. Ti^{4+} substitutes for Mg^{2+} in octahedral sites but does not replace Si^{4+} in tetrahedral sites. The solubility of Ti^{4+} is very small at 600°C, 1 kbar (0.07 Ti atom per formula unit); it increases up to 0.2 atom/f.u. at 800°C, 1 kbar, and to 0.7 atom/f.u. at 1000°C, 1 kbar. Pressure reverses this trend and reduces solubility (0.2 Ti/f.u. at 1000°C, 7 kbar). The results of this study have been compared with data on natural occurrences: Ti content of ferromagnesian micas increases with increasing grade of metamorphism, and with increasing bulk-rock solidus temperature in igneous assemblages.

SEDIMENT GEOCHEMISTRY IN LAKES NEAR SUDBURY, ONTARIO

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Sixty-five surface sediment samples were collected from lakes in the NE Sudbury district (46°15′ - 47°30′N; 79°30′ - 81°30′W). Sediment samples frozen in the field were freeze-dried and ground to -200 mesh for all chemical determinations. Sediment analysis included heavy metals (Ni, Cu, Zn, Pb, Cd, Fe, Mn), organic carbon, total nitrogen, acid-extractable phosphorus and particle size distribution. Results indicated significant concentrations of Ni and Cu in the surface sediments, with a well-defined gradient increasing towards Sudbury. The other heavy metals paralleled this pattern, but were not as explicitly outlined. Factor analyses suggested a strong Ni, Cu (distance from Sudbury)$^{-1}$ relationship as well as a secondary Fe-Mn-pH-Eh relationship operating within the sediments. Despite high organic carbon concentrations in the sediments (up to 37% dry wt. organic C), there is no apparent correlation with the heavy metals. From limited particle size data, all the sediments were classified as silty clays or clayey silts. Again, no increased metal content would be correlated with sediment particle size. An acid-available phosphorus-total iron association in the sediments was observed to be highly dependent on the Eh status of the lake sediments. Heavy metal data from the lake waters correlate with the gradient for Ni/Cu in the sediments. A fractionation study of heavy metals in atmospheric fall-out, lake water and lake sediments suggested the importance of the lake water chemistry (pH, alkalinity) in determining relative abundances of metals in the water and sediment portions.

GEOCHEMICAL VARIABILITY OF BOTTOM SEDIMENTS IN NEWFOUNDLAND INLETS

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Analysis of 76 surface sediment samples from four Newfoundland inlets indicates grain size is a major factor regulating geochemistry because proportions of silicate and non-silicate components vary with size. Concentrations of total Cu, Pb, Zn, Cr, Co and Ni increase with increasing clay content, but for most of these elements smaller concentrations are associated with the clay-size than the coarser fraction. Plots of trace element concentration/clay content ratio vs. clay content discriminate between concentrations in both fractions and filter out the grain size effect.

Such plots are particularly applicable to studies of (1) marine prospecting for economic minerals (2) provenance of fine-grained marine sediment and (3) possibly environmental geology. For the first case, examples are given of Cu/clay, Pb/clay and Cr/clay anomalies for marine sediments near to onshore mineralized bedrock. For the second case, fine-grained sediments, which on the basis of mineralogy alone are similar in each inlet and on the adjacent shelf, can be differentiated by trace element/clay ratios (particularly for Co and Pb). Such differences, though subtle, probably reflect variations in trace-element concentrations of the source rocks and thus suggest the sediments are locally derived.

FLUORITE-DAWSONITE RELATIONSHIPS AT A NEW MONTREAL LOCALITY

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Dawsonite and fluorite, crystallized together, have been collected from the excavation for a new portion of the Trans-Canada Highway going underground through downtown Montreal. This occurrence appears to be associated with a continuation of the feldspathic dyke of the original Montreal locality. The hydrothermal origin of the Montreal dawsonite, which has recently been questioned, is reaffirmed on the basis of field and petrographic studies of the new material. Similar specimens of dawsonite and fluorite occurring together have also been collected recently at Mont St. Hilaire, Que., and Mont St. Bruno, Que.

PHOSPHATE MINERALS FROM THE YUKON TERRITORY, CANADA

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A phosphate mineral assemblage has been found in a Cretaceous sideritic iron-formation in the Big Fish-Blow Rivers area of the Yukon Territory. The minerals occur in fractures produced by the folding of the beds. The absence of intrusive bodies and the apparent lack of metamorphism indicate a relatively low temperature of formation of the minerals. Some of the phosphates have been found only in pegmatites prior to the discovery of this occurrence. The species identified so far are: lazulite, brazilianite, augelite, wardite, childrenite, ludlamite, vivianite, and arrojadite. Six minerals, which may be new species, are under study. The lazulite, wardite, and arrojadite are exceptional representatives of their species as they occur in very large, well-developed crystals.

Magnesium plays a significant role in the chemistry of the minerals. One analyzed vivianite, for example, has almost half of the iron replaced by magnesium. The magnesium analogue of vivianite may be present.

EXPERIMENTAL MODELLING OF INTERELEMENTAL RELATIONSHIP IN NATURAL FERROMANGANESE MATERIALS

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Metallic hydroxides of Fe and Mn constitute an important fraction of natural unconsolidated sediments. Because of their ability to incorporate a number of trace elements, they are potential factors in elemental mass transfer. In an attempt to understand the role of aqueous media and the nature of interelemental relationship within the multicomponent hydroxides — which occur as coatings on sediments, particulates of suspended matter and ferromanganese materials in recent sediments — an experimental investigation was made on multiple hydroxide coprecipitation of Fe, Mn and Ni from aqueous media of varying ionic strength. The coprecipitates were studied with the aid of several analytical tools such as infra-red spectra, Mössbauer effects and scanning electron microprobe. Based on these results, it is concluded that the mixed-hydroxide precipitates form a continuous non-ideal solid solution with $Fe(OH)_3$, $Mn(OH)_2$ and $Ni(OH)_2$ as the end members. Free energies of mixing calculated from the experimental data indicate that the mixed hydroxides are stable relative to the end members. Depending on the ionic strength of the aqueous media, the mixed hydroxides have a certain amount of exchange capacity and other trace elements such as Co and Cr in the aqueous media can occupy these exchange sites. Such an experimental model can be used to satisfactorily explain the interelemental relationship reported by several workers for natural ferromanganese materials.

FACTORS AFFECTING THE SYNTHESIS OF CRYPTOCRYSTALLINE STRENGITE FROM AMORPHOUS IRON OXYHYDROXIDE

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Four experiments were initiated to examine the effects of pH, Eh (dissolved oxygen), agitation and concentration of key reactants (Fe and P) on the reaction of P with amorphous iron oxyhydroxide under conditions encountered in natural systems. pH and dissolved oxygen content are the most important variables controlling initial P uptake in the aqueous phase. The pH range (4-7) is optimal for uptake when Fe is greater than 0.25 mg/*l* and dissolved oxygen concentration is $>15\%$ saturation. Digestion of the resultant iron oxyhydroxide-phosphate under conditions of neutral pH, oxidizing EH and $T = 100^\circ$, produced a mixture of cryptocrystalline strengite and metastrengite. This end-product verifies the thermodynamic predictions of Nriagu (1972).

TRACE ELEMENT GEOCHEMISTRY OF PISTON CORES FROM WESTERN MICHIGAN COASTAL LAKES

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Twenty-five cores from 100 to 320 cm in length from western Michigan coastal lakes were analyzed for Cr, Cu, Zn, and Mn, organic fraction, and sediment size. Lakes included in the study were Spring Lake, White Lake, Muskegon Lake, and Lake Macatawa and represent areas of high and low industrial development. Industrialization is indicated by increases in Cr, Cu, and Zn concentrations toward the tops of most cores. Various industrial events of known time and origin can be correlated between cores and are used to establish sediment accumulation rates. Sedimentation rates vary between lakes and average from 0.5 to 3.0 cm/year.

Natural background concentrations of trace elements vary between core locations and within a given core and are apparently altered slightly by natural phenomena. Relative background concentrations of Cr, Cu, and Zn compare favorably with those of other areas. Enrichment of Cr, Cu, and Zn and changes in relative proportions of these elements reflect contamination by aerosols and/or industrial effluent. Aerosol contamination levels for the region are reflected by trace metal enrichment within near-surface sediments collected from Spring Lake, which has no industry.

Interpretation of trace element enrichment zones within sediment cores is dependent upon establishment of background levels for specific locations, determination of relative aerosol concentrations for the region and sediment analysis of cores.

MODIFICATION OF THERMAL REGIME OF LOWER CRUST VIA PENETRATIVE CONVECTION

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In regions of extensive volcanic activity it is to be expected that the thermal structure of the lower crust would be altered as a result of repeated penetration by mantle-derived magmas. The amount of heat lost in transit by an individual magma body is a complex function of the initial magma temperature, size of the magma body, rate of ascent, temperature of the surrounding crust, and the convective heat-transfer coefficient between magma and crust. While the exact nature of heat transfer is not amenable to solution, it is possible to estimate the heat lost in transit by comparing the heat content of the magma when it penetrates the base of the crust to the heat content at eruption. Combination of such estimates with estimates of magma flux makes it possible to evaluate heat generation per unit time due to penetrative convection. Results indicate that magmatic activity on the level of that observed in Japan does not sigificantly raise the temperature of the crust. At depths of 35 kilometers, temperature is rased only 10°-15°C. after 5 million years of volcanic activity. Since lava flux observed on the surface is clearly less than that which penetrates the lower crust, temperature profiles for magma flux 10 and 20 times that observed in Japan are calculated. Results indicate that 50° and 100° of crustal heating would be achieved by such levels of activity. Applications to melting in the lower crust and a subsequent model for the generation of batholiths is developed.