



## Geochemistry of Natural Waters

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The International Symposium on the Geochemistry of Natural Waters, held under the auspices of the IAGC and IAHS from August 18 to 22, 1975, at the Canada Centre for Inland Waters in Burlington, Ontario, was co-sponsored by the Centre and by the U.S. Geological Survey.

The Symposium was preceded by a field trip, August 11 to 16, arranged by Dr. J. R. Kramer from McMaster University. From Hamilton, the participants travelled via Manitoulin Island to Sault Ste. Marie and then returned by way of Elliot Lake and Sudbury.

Over one hundred scientists from sixteen countries, but with the majority from the United States and Canada, took part in four and a half days of formal sessions and informal evening meetings. Financial restrictions on travel prevented the attendance of several speakers. A considerable amount of shifting of speakers and several impromptu contributions resulted in a full program.

There were four sessions: analytical methods for geochemical studies of natural waters; interlaboratory comparisons of analytical methods; geochemical and mathematical models of surface and ground water systems; and unpolluted waters.

Because of the present mail strike, most of the expected contributions from the session chairmen have not been received. The author wishes to acknowledge those of A. E. Ellis and D. Langmuir from which he has freely borrowed.

Before the formal sessions, several general talks were given. Professor M. G. Valyashko, Chairman of the IAGC Working Group on the Geochemistry of Natural Waters, welcomed the participants and reviewed in his talk the progress made on water geochemistry and the background to the Symposium. Dr. J. Da'Costa of UNESCO described the current activities of this organization in the field of water chemistry, pollution and the modeling of water bodies.

H. Golterman reviewed the factors controlling the development and growth of algae in estuarine environments with particular reference to the cycling of nitrogen and phosphorous through sediments and water. M. Dall'Aglia discussed work on earthquake prediction through the monitoring of deeply circulating waters (e.g., thermal waters) for helium, radon and other trace elements that could indicate changing rock-water interactions.

In Session One, most papers were concerned with the systematic development of field collection, storage and analysis of fresh and sea water samples. These papers described improvements to specific analytical methods, automated field collection methods, procedures for the extraction and identification of trace organic materials in water and systematic studies of factors leading to contamination during collection and storage of water samples for trace element analysis. A definitive paper was presented by Nishimura *et al.* on adequate sampling and analysis of mercury in natural waters. They found that polyethylene bottles give irregularly high values for mercury, that it is necessary to add sodium chloride as well as acid to prevent adsorption of mercury on bottles, and that the mercury value determined by the reduction method with stannous chloride increases gradually during storage of an acidified seawater sample until a constant value is reached after a few weeks.

In Session Two, A. J. Ellis and M. W. Skougstad summarized the results from the IAGC International comparative water analysis program involving seven natural waters of varying composition and the extensive program on interlaboratory testing of water samples in the Water Resources Division of the USGS, respectively. With suitable care in sample preparation and container

choice, there were few problems with sample stability for most non-volatile and biologically inactive elements. In general the laboratories involved reported reasonable results for most common water constituents. The most common source of error was the incorrect application of an analytical method rather than the choice of an inappropriate method. For trace metals at the tens of microgram per litre level, the poorest quality results were for As, Co, Cd, Cr, Pb, Ni and Zn.

C. C. Patterson gave a detailed account of the difficulties involved in analyzing for lead in the nanogram per litre range, which is the natural level for lead in seawater. Only if scrupulously clean laboratory techniques were used, containers were cleaned using rigid specifications and collection equipment was protected from contamination could consistent results be obtained.

K. Sugawara summarized the development of analytical standard solutions for seawater chemistry and the international comparison studies on nutrient elements and trace metals in seawater. Mercury and cadmium analyses especially had a very high coefficient of variation. Different forms of mercury in seawater were apparently responsible for the variation in the analytical results with the type of sample pretreatment.

From the discussion, it was clear that the determination of elements at levels less than a microgram per litre was a complex and expensive procedure and that programs should not be lightly entered into. There was agreement on the desirability of keeping more than one analytical method operating for any element.

In Session Three, most of the talks dealt with geochemical models. Y. K. Kharaka discussed the utility and limitations of solution-mineral equilibrium models. The major uncertainties in these models are likely to be the amount and quality of the thermodynamic data available for the computations of equilibrium constants, the reliability of chemical analyses and the extrapolation of the measured pH to the *in situ* pH of the sample.

D. DiToro pointed out that in modeling geochemical systems, species can be considered to be at equilibrium only if the reactions occur very rapidly. Otherwise the behaviour of the system is controlled

by mass transport caused either by advection or by dispersive mixing.

The remainder of the papers dealt with geochemical models based on specific situations. Among them were papers on nutrient regeneration from sediments in polluted lakes, the relationship between surface water chemistry and the weathering of rocks and soils for a drainage basin in Wyoming. Other papers dealt with the relationship between the regional geology of the USA and major stream water types, the thermal springs of Tuscany, the waterways of the Louisiana coastland areas, the water and solute balance in Lake Chad using isotopic tracers, and the organic carbon and nitrogen concentrations and loadings of five rivers in the USA. In Norway, a study of 155 lakes is being carried out to study the interactions of meteorological, geological and biological processes.

It was suggested by R. D. Schuiling that pre-pollution levels of elements in certain rivers could be estimated through calculating erosion rates from the transport of major rock-forming elements in waters, and knowledge of the composition of the major rock types. The study referred in particular to the Rhine.

R. Kilham in his discussion of the chemistry of African Lakes pointed out that their composition is determined by the circumstances that atmospheric precipitation is relatively small and that the evaporation-crystallization process produces sodium bicarbonate-carbonate lakes containing little calcium, thereby deviating from the evolutionary pathway for natural waters suggested by Gibbs.

F. Schwille's talk was concerned with man's influence on underground water quality, and reviewed the microbial and chemical processes occurring when water containing dissolved organic carbon, phosphate and nitrate passed through an underground aquifer with loss of oxygen and production of objectionable reduced solution species. Hydrological models were discussed to enable optimum use of aquifer systems both in disposal and water supply situations, taking into account both rates of reaction as well as chemical equilibrium concepts. Specific element studies included the redistribution and reaction of mercury and of fluoride in ground waters, and the genesis of

constituents in sub-surface thermal and mineralized waters.

In the final session, two unscheduled talks were given. P. Kilham discussed fluoride in African rivers and W. Graustein the effects of vegetation on the chemistry of rain.

G. Brunskill described the rates of transport of dissolved major elements in the MacKenzie River system. He concluded that chemical erosion in the western arctic and sub-arctic region of Canada is in the same range as that in the temperate zone.

V. C. Kennedy described his work on the variation of some dissolved inorganic constituents with stream discharge in the Mattole River in California. The seasonal pattern is related to the well-defined winter rainy period and depends on the varying contributions of overland flow, seepage and ground-water flow.

The dissolved inorganic and organic carbon distribution in Minnesota rivers was described by W. Maier. Seasonal DOC variations were inversely related to stream flow, suggesting that most of the DOC was from natural sources. The organic carbon content has decreased from around 20 mg/l in 1968-69 to around 7 in 1973-75.

A fascinating example of a very concentrated tropical brine pond where the temperature increased with depth due to the trapping of solar radiation and the major cation reached saturation concentration in the lower hot and anaerobic layer was given by A. Turek.

Other papers were on studies of estuarine mixing using  $O^{18}/O^{16}$ , on the geochemistry of ammonia in the Hudson River estuary, on trace elements off the South African coast, and on the effects of suspended sediment transport in a river contaminated by tailings from a major copper mine near Bougainville, New Guinea. Groundwater chemistry was represented by paper on the distribution of gases in surface and groundwater and on the water chemistry in weathered Deccan basalts in India. B. C. Raymahaskay explained that the groundwater chemistry is controlled by chemical equilibria involving precipitation of calcite and the alteration of augite and calcium plagioclase to calcium montmorillonite and kaolinite.

In conclusion, the Symposium was highly successful in bringing together water chemists and geochemists from a wide range of organizations. The

coverage of the program enabled participants to obtain a broad review of water geochemistry as well as to discuss work in their own specialty.

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