## References and Notes

1. H. A. Pohn and R. L. Wildey, *U.S. Geol. Surv. Prof. Pap. 599-E* (1970).
2. D. E. Wilhelms and J. F. McCauley, geologic map of the near side of the moon, *U.S. Geol. Surv. Map I-703* (1971); F. El-Baz, in *NASA Spec. Publ. 289* (1972), p. 25-66; M. H. Carr, in *ibid.*, p. 25-63.
3. T. N. V. Karlstrom, J. F. McCauley, G. A. Swann, U.S. Geological Survey open-file report (1968); J. F. McCauley, *Trans. Amer. Geophys. Union* **50**, 229 (1969); D. H. Scott and N. J. Trask, *U.S. Geol. Surv. Prof. Pap. 599-I* (1971).
4. F. El-Baz and A. M. Worden, *NASA Spec. Publ. 289* (1972), p. 25-1.
5. T. R. McGetchin, M. Settle, B. Chouet, *Trans. Amer. Geophys. Union* **53**, 533 (1972); *J. Geophys. Res.*, in press.
6. S. S. C. Wu, F. J. Schafer, R. Jordan, G. Nakata, J. Derick, in *NASA Spec. Publ. 289* (1972), p. 25-36; U.S. Army Topographic Command, preliminary topographic map of the Apollo 17 landing area (1 : 50,000; zone 36) (July 1972).

7. Research supported by NASA grants NGR-22-009-522 and NGR-22-009-637, by the U.S. Geological Survey under NASA contract T5874A (T.R.M.), and by Bell Telephone Laboratories under NASA contract NASW-2377 (J.W.H.). Publication authorized by the director, U.S. Geological Survey.

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# Mechanisms of Trace Metal Transport in Rivers

Abstract. *Trace metals transported by the Amazon and Yukon rivers were analytically partitioned among the transport phases: in solutions, ion exchange, organic materials, metallic coatings, and crystalline solids. The distribution for both rivers is similarly proportioned, with copper and chromium transported mainly in the crystalline solids, manganese in coatings, and iron, nickel, and cobalt distributed equally between precipitated metallic coatings and crystalline solids.*

It is necessary to know the mechanisms of the transport of trace metals in rivers in order to be able to understand their chemical cycles in nature. This knowledge is indispensable in evaluating the fate of trace metals that man, as a polluter, superimposes on the natural system. From the public health viewpoint it is important whether the trace metals are (i) in solution or adsorbed on solids, where they are readily available; (ii) in organic materials or metallic hydroxides, where chemical changes are required before they are released, so that they are less available; or (iii) in the crystal structures of suspended materials, where they are nearly unavailable in nature.

Numerous workers (*1*) have studied trace elements in sea water, especially in the cores of bottom sediments and in manganese nodules. Jenne (*2*) reviewed the status as of 1968 of the chemistry of trace metals in soils, sediments, and freshwaters, pointing out the need for studies of the relative affinity of organic matter compared with iron and manganese oxides for trace elements in stream sediments. Since then, Turekian and co-workers (*3*) have studied the dissolved Ag, Sb, Cr, Co, Rb, Cs, Se, and Mo in several streams, and have conducted adsorption experiments with American Petroleum Institute clay minerals standards in order to calculate the amounts of the metals adsorbed and released in seawater. They also filtered the suspended material (with a filter of pore size 0.45 μm) and analyzed the bulk samples for Cr, Ag, Mo, Ni, Co, and Mn.

In the present study I attempted to evaluate the amounts of Fe, Ni, Cu, Cr, Co, and Mn actually transported by rivers (i) in solution, (ii) by adsorption, (iii) in solid organic material, (iv) as metallic coatings, and (v) in detrital crystalline material.

All the samples of water and suspended sediments obtained for the study reported here were taken from the Amazon and Yukon rivers, at 60 percent of the depth in the main channel, upstream of any influence from salt water; this ensured that the samples were indicative of river transport. The samples from the Amazon River were taken off Macapá, Brazil; those from the Yukon River were taken upstream from Alakanuk, Alaska. All the samples were filtered under pressure within 2 hours after sampling; the filters (pore size, 0.45 μm) had been washed with filtered river water (*4*). The filtered water samples were acidified with redistilled HCl to *p*H 1.5 and stored in polyethylene bottles previously washed with redistilled HCl. The filtered residue was stored on the filter, preserved with a volatile organic solution (*5*).

The trace metals in solution in the filtered water samples were concentrated by complexing with ammonium pyrrolidine dithiocarbamate, followed by solvent extraction with methyl isobutyl ketone (*6*). The adsorbed cations were removed from the suspended material by using a 1*N* $MgCl_2$ solution (*p*H 7). To ensure that none of the suspen-

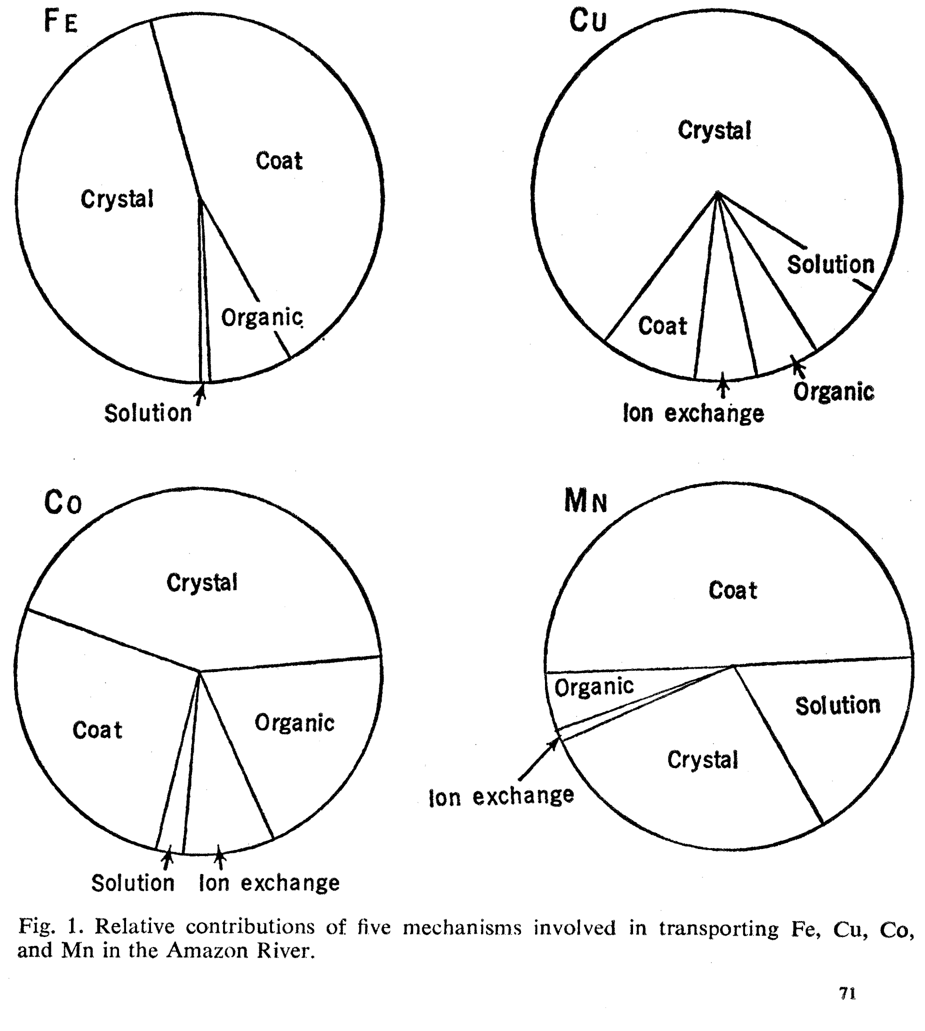

Fig. 1. Relative contributions of five mechanisms involved in transporting Fe, Cu, Co, and Mn in the Amazon River.

Table 1. Percentages of the total amounts of Fe, Ni Co, Cr, Cu, and Mn transported by five mechanisms in the Yukon and Amazon rivers.

| Mechanism | Fe | Ni | Co | Cr | Cu | Mn |
|---|---|---|---|---|---|---|
| *Amazon River* | | | | | | |
| 1) In solution and organic complexes | 0.7 | 2.7 | 1.6 | 10.4 | 6.9 | 17.3 |
| 2) Adsorbed | 0.02 | 2.7 | 8.0 | 3.5 | 4.9 | 0.7 |
| 3) Precipitated and coprecipitated | 47.2 | 44.1 | 27.3 | 2.9 | 8.1 | 50 |
| 4) In organic solids | 6.5 | 12.7 | 19.3 | 7.6 | 5.8 | 4.7 |
| 5) In crystalline sediments | 45.5 | 37.7 | 43.9 | 75.6 | 74.3 | 27.2 |
| *Yukon River* | | | | | | |
| 1) In solution and organic complexes | 0.05 | 2.2 | 1.7 | 12.6 | 3.3 | 10.1 |
| 2) Adsorbed | 0.01 | 3.1 | 4.7 | 2.3 | 2.3 | 0.5 |
| 3) Precipitated and coprecipitated | 40.6 | 47.8 | 29.2 | 7.2 | 3.8 | 45.7 |
| 4) In organic solids | 11.0 | 16.0 | 12.9 | 13.2 | 3.3 | 6.6 |
| 5) In crystalline sediments | 48.2 | 31.0 | 51.4 | 64.5 | 87.3 | 37.1 |

sion was lost or would contaminate the absorbed extract, dialyzing tubes were used to remove the solute. The adsorbed ions were released in the first few minutes, after which the rate of release became negligible. Tests to determine whether the metallic coatings would be dissolved showed that the coatings were not affected by the extracting solution. Ammonium acetate, the standard adsorption extractor, was tested as an extracting solution and was found unsatisfactory because it dissolved or complexed the metallic coatings of the sediment particles. The metallic coatings on the suspended material were removed by reducing the metals with sodium dithionite and complexing them with citrate; the complexed metals were then separated from the suspended material by dialysis. The solid organic material was oxidized by sodium hypochlorite (*p*H 8.5); the liberated metals were then reduced, complexed, and separated by dialysis. The remaining crystalline detritus of the suspended material was fluxed with lithium metaborate at 1000°C and dissolved in $HNO_3$. All extracted solutions were analyzed with an atomic absorption spectrophotometer (Instrumentation Laboratory, model 153) (*7*).

The chemical mechanisms that must be considered in studying the transport of trace metals in rivers involve:

1a) Dissolving of ionic species and inorganic associations.

1b) Complexing with organic molecules in solution.

2) Adsorption on solids.

3) Precipitation and coprecipitation on solids (metallic coatings).

4) Incorporation in solid biological materials.

5) Incorporation in crystalline structures.

This study was designed to specifically determine the amounts of the trace metals transported in rivers by each of these mechanisms. The first two mechanisms are considered as a combined factor in this report because they have not yet been distinguished analytically. The analysis involves differentiating the material passing through the molecular filter into fractions of various molecular weights and then analyzing each fraction for trace elements.

The results of the analysis are compiled in Table 1, which shows the percentages of total Fe, Ni, Co, Cr, Cu, and Mn transported by the five mechanisms. Figure 1 shows the relative contributions of the five mechanisms in transporting four of the trace metals in the Amazon River. Similar results were obtained for all the trace metals in both the Amazon and the Yukon. This similarity is particularly interesting since the two rivers are in extremely different climates and since both are large unpolluted rivers.

A detailed examination of the mechanisms responsible for transporting each of the metals analyzed reveals several interesting relationships. Precipitated metallic coatings transport 40.6 percent of the total Fe transported in the Yukon River and 47.2 percent of the total Fe transported in the Amazon River. The crystalline particles of the sediments transport 45.5 and 48.2 percent of the total Fe carried by the Amazon and Yukon rivers, respectively. These two mechanisms—involving metallic coatings and crystalline particles—therefore account for 92.7 percent (Amazon) and 88.8 percent (Yukon) of the total Fe transported. Incorporation of the iron into the solid biological material carried by the rivers, which accounts for 6.5 percent (Amazon) and 11 percent (Yukon) of the total Fe transported, is of secondary importance. The remaining chemical mechanisms of transport—in solutions and by adsorption—are of almost no significance in the transport of Fe by the two rivers.

The mechanisms important in the transport of nickel are the same as those important for Fe. Precipitated and coprecipitated metallic coatings and the crystalline particles of the sediments together account for 82 percent of the total Ni transported by the Amazon River and 79 percent of the total Ni transported by the Yukon River. The third most important mechanism for Ni is incorporation into the solid biological material, which transports 13 and 16 percent of the total Ni carried by the Amazon and Yukon rivers, respectively. The remaining 5 percent of the Ni transported by each of the rivers is distributed equally between solution and adsorption on solids.

Most of the Cu and Cr transported in the Amazon and the Yukon is carried in the crystalline particles of the sediments (Table 1 and Fig. 1). The distribution of Co between the transport mechanisms appears to be intermediate between the distribution of the Cu-Cr pair and that of the Fe-Ni pair, with the crystalline sedimentary material carrying about half of the total Co transported. Precipitation and coprecipitation in metallic coatings and incorporation into solid biological material are the second and third major transport mechanisms for Co. The remaining mechanisms are responsible for transporting less than 10 percent of the total Co carried by the two rivers.

The transport mechanisms for Mn differ slightly from those for the other five metals. Metallic coatings account for most of the Mn transported in the Amazon and the Yukon (Table 1 and Fig. 1). Incorporation in the crystalline particles and transport in solution are second and third in importance.

The first conclusion that can be drawn from the data reported here is that no sweeping generalization can be made regarding the transport mechanisms for trace metals in rivers. The mechanisms responsible for transporting the metallic elements varied for the six metals studied in the samples from two unpolluted large rivers, the Amazon and the Yukon.

Incorporation into the crystalline structures of the sediments is the major transport mechanism for Cu, Co, and Cr carried in the two rivers and is second most important for Fe, Mn, and Ni. This mechanism is controlled by the composition of the crystalline material carried by the river; in turn, the composition of the crystalline material is dictated by the composition of the rocks of the river's drainage basin.

The second most important mechanism is precipitation and coprecipitation of the metals in the metallic coating on the particles. For Fe, Mn, and Ni this is the major mechanism of transport, and for Co it is second most important. It is probable that the Ni, Co, and Mn are coprecipitated with the much larger amounts of Fe found in the coatings.

Transportation of trace metals in solution accounts for a significant percentage (up to 17 percent) of the total carried only in the case of Mn. Theoretically, the stable form of Mn in the normal oxidizing conditions and *p*H (5 to 7) of the rivers is solid $MnO_2$ and should not be the soluble form, $Mn^{2+}$ (*8*). It is possible that the Mn analyzed in solution may have been in very small solid particles; however, this is unlikely since filtering water through 0.1-$\mu$m filters resulted in the same retention and concentration of Mn as filtering it through 0.45-$\mu$m filters. Also, it would seem fortuitous that only the Mn was fine enough to pass through the filters while none of the other five trace metals did. Other possibilities are that the Mn was complexed with organic molecules or was associated with inorganic molecules.

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### References and Notes

1. D. C. Lynn and E. Bonatti, *Mar. Geol.* **3**, 457 (1965); B. J. Presley, R. R. Brooks, I. R. Kaplan, *Science* **158**, 906 (1967); D. E. Robertson, *Geochim. Cosmochim. Acta* **34**, 553 (1970); J. F. Slowey and D. W. Hood, *ibid.* **35**, 121 (1971); K. K. Turekian, *ibid.* **32**, 603 (1968); R. R. Turner and R. C. Harriss, *Deep Sea Res.* **17**, 633 (1970).
2. E. A. Jenne, in *Trace Inorganics in Water* (American Chemical Society, Washington, D.C., 1968), pp. 337–387.
3. K. K. Turekian and M. R. Scott, *Environ. Sci. Technol.* **1**, 940 (196 → K. K. Turekian, R. C. Harriss, D. G. Johnson, *Limnol. Oceanogr.* **12**, 702 (1967); D. P. Kharkar, K. K. Turekian, K. K. Bertine, *Geochim. Cosmochim. Acta* **32**, 285 (1968).
4. After the filtration at 0.45 $\mu$m, several samples from each river were filtered at 0.1 $\mu$m in order to determine whether any finer material was passing through the coarser filter. The first 10 percent of the water sample was filtered before a portion was taken for analysis. By this procedure the filtering device and filter were washed and the filter became partially clogged, materially reducing the effective pore size. The analytical results on the filtered water showed no significant difference between water filtered with 0.1-$\mu$m pore size and water filtered with 0.45-$\mu$m pore size.
5. S. H. Hutner and C. A. Bjerknes, *Proc. Soc. Exp. Biol. Med.* **67**, 393 (1948).
6. S. Sprague and W. Slavin, *At. Absorp. Newslett.* **20**, 11 (1964).
7. *Procedure Manual for Atomic Absorption Spectrophotometry and Instruction Manual* (Instrumentation Laboratory, Inc., Lexington, Mass., 1969).
8. J. J. Morgan and W. Stumm, *Proc. 2nd Int. Water Pollut. Conf. Tokyo* (1964), p. 103.

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# Kilauea Volcano, Hawaii: A Search for the Volcanomagnetic Effect

Abstract. *Brief excursions of magnetic field differences between a base station and two satellite station magnetometers show only slight correlation with ground tilt at Kilauea Volcano. This result suggests that only transient, localized stresses occur during prolonged periods of deformation and that the volcano can support no large-scale pattern of shear stresses.*

For many years investigators, particularly in Japan, have surmised the existence of a volcanomagnetic effect in the form of transient magnetic anomalies associated with eruptions (*1*). Measurements made with a pair of interconnected proton magnetometers on Ruapehu and Ngauruhoe volcanoes in New Zealand (*2*) encouraged the hope that magnetometry might provide a tool for predicting eruptions. Kilauea Volcano, Hawaii, appeared to offer a particularly favorable area for observations of this kind because of its frequent eruptions, the highly magnetic, basaltic rocks found in the area, and the proximity of the Hawaiian Volcano Observatory as a logistic basis for the operation of an instrumental array. We therefore planned a collaborative program using a network of three total-field magnetometers, with a base station linked by radio to two satellite stations. We now have 12 months of records, which, although broken, lead us to the tentative conclusion that stress-strain effects accompanying eruptions of Kilauea are different from those of the New Zealand volcanoes.

Except for a 3-month period, the base station sensor has been located at the Uwekahuna Vault, close to the observatory; during July through September 1971 it was at the Outlet Vault, which was engulfed by lava during the September 1971 eruption. The satellite sensors are located near Pauahi Crater and Puu Honuaula, 10 and 43 km, respectively, along Kilauea's east rift zone from Uwekahuna (Fig. 1). The total field at the base station is recorded every minute, and differences in field strength between the base station and each satellite are recorded on alternate minutes. The difference field readings are obtained by applying a 1-Mhz signal to the "up" and "down" inputs of reversible counters, with inputs gated by 1024 cycles of the two simultaneous proton frequencies to be compared. The readings are obtained as printed paper tape for immediate examination and magnetic tape for computer processing. The instrumental resolution is 0.05 gamma, but trials with closely spaced sensors gave difference field readings having a standard deviation of 0.2 gamma, and this has been achieved also for hourly periods during magnetically quiet times over the Hawaii network. Although we discriminate against magnetic disturbances of remote origin by taking differences, because of the proximity of seawater in which electric currents are induced by geomagnetic variations, a diurnal variation of 10-gamma amplitude appears in the record of Puu Honuaula minus the base station but there is only a 1-gamma amplitude variation in the record of Pauahi minus the base station. However, the standard deviations of daily averages are less than 1 gamma in both cases.

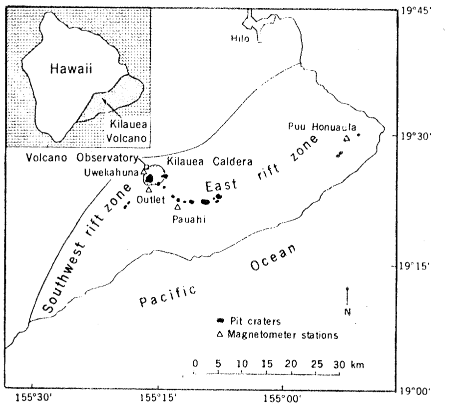

Fig. 1. Location map showing major structural and eruptive features of Kilauea Volcano with sites of the magnetometer sensors.

A program of tilt and strain measurements on Kilauea is well developed (*3*) and shows pronounced inflation of the summit region before eruptions and deflation during flank eruptions. We supplemented the tiltmeter network by installing in the Outlet Vault a continuously recording mercury level tiltmeter (*4*), and a commercial instrument of the same design (*5*) was added by J. M. W. Rynn of the Lamont-Doherty Geological Observatory. Both tiltmeters were destroyed during the September 1971 eruption. The presumption upon which our experiment was based is that the strains indicated by