

GEOCHEMICAL STUDIES IN THE URANIUM PROSPECT AT UMRA, RAJASTHAN

I. Geochemistry of Waters

BY V. V. S. S. TILAK AND U. ASWATHANARAYANA

(Department of Geology, Andhra University, Waltair)

Received October 31, 1962

(Communicated by Prof. T. N. Muthuswami, F.A.Sc.)

ABSTRACT

With the objective of investigating the geochemistry of the natural waters of the uranium prospect at Umra, Rajasthan, the concentrations of uranium, nickel, cobalt, copper, vanadium, etc., in the natural waters have been determined and their distribution patterns have been interpreted in the light of the geology of the area, the climatic and hydrological conditions prevalent there and the geochemical behaviour of the elements concerned. It is found that there is a marked contrast in the uranium content of winze and well-waters. The presence of copper in waters despite their high pH is ascribed to the tendency of copper to form colloidal suspension of basic carbonates. The observation, that vanadium is present in the secondary uranium-vanadium minerals but is absent in the waters, could be explained in the light of the geochemical behaviour of the element. The concentration of cobalt in most of the water samples and its absence in some is traceable to the controlling effect of pH on the mobility of cobalt. Nickel in waters might have been 'scavenged' and absorbed on hydrated iron oxides, which explains the absence of nickel in waters. Mention is made of the health hazard involved in drinking water from one of the wells with high content of uranium.

INTRODUCTION

THE pattern of secondary geochemical dispersion of an element in natural waters in an area depends upon the geology of the area (nature and extent of geological formations, structural features, etc.), climatic and hydrological conditions (magnitude and distribution of rainfall, temperature, depth of the water-table, etc.), geochemical factors (hydrogen-ion concentration, oxidation potential, solubility of salts, coprecipitation, sorption, colloidal solutions, formation of complexes, etc.) and chemical nature of the element. The

objective of the present study is to investigate the pattern of distribution of uranium, nickel, cobalt, copper, vanadium, calcium, sodium and potassium in the natural waters (well, stream and mine waters) in and around the Umra uranium prospect, Rajasthan, and to delineate their interrelationships and the factors controlling their dispersion in aqueous environment in this area. An analysis of data obtained in this study may be of help in geochemical prospecting for U, Cu, etc., in the area.

GEOLOGICAL SETTING

The stratigraphical succession of the uranium belt is as follows:

Delhi System	Alwar Series	{ Quartzites Conglomerates
Pre-Delhi	(Post-Aravalli)	Granite
Aravalli System		{ Limestones Carbonaceous Shales Quartzites Phyllites and biotite schists Epidiorites, etc.

The limestones and shales have a NE-SW strike and dip 50-70° to the SE. The pattern and controls of mineralisation of uranium and copper at the Umra prospect were studied by Dar and Nandi (1958). Both structural and lithologic controls of mineralisation could be recognised here. The Aravallis here were folded and overturned to the west. The black shales which form a part of the Aravalli sequence suffered severe isoclinal folding and contortion, and developed cleavage. The uranium ore occurs as veins and infillings in fractures and shears in the sheared contact zone between the black shales and "passage bed" (grey chloritised shales and phyllites that occur between black shales and impure limestones). The distribution of ore lenticles or pods, which vary in length from less than 1 foot to 25 feet, is sporadic. The uranium ores consist of uraninite and pitchblende (primary), gummite, carnotite, tyuyamunite, torbernite, metatorbernite, autunite and uranophane (secondary).

Two types of quartz veins—one consisting of milky white quartz with magnetite and ilmenite and the other consisting of translucent greyish quartz with kyanite—are found to intrude into the Aravallis here.

At Umra, mining activity is in progress in an area of roughly two square miles. The mine area is divided into four grids (I to IV) for convenience and consists of six adits, five shafts and two drives. Lithologically, two

broad zones could be recognised in the mine area—the impure limestone zone and the phyllites-limestone zone. The grids comprise of the following:

Grid No. I	Adit IV and Shaft V	} Zone of phyllites and limestones
Grid No. II	Drives I and II and Shaft II	
Grid No. III	Adits I, II and III and Shaft IV	} Impure limestone
Grid No. IV	Adits V and VI	

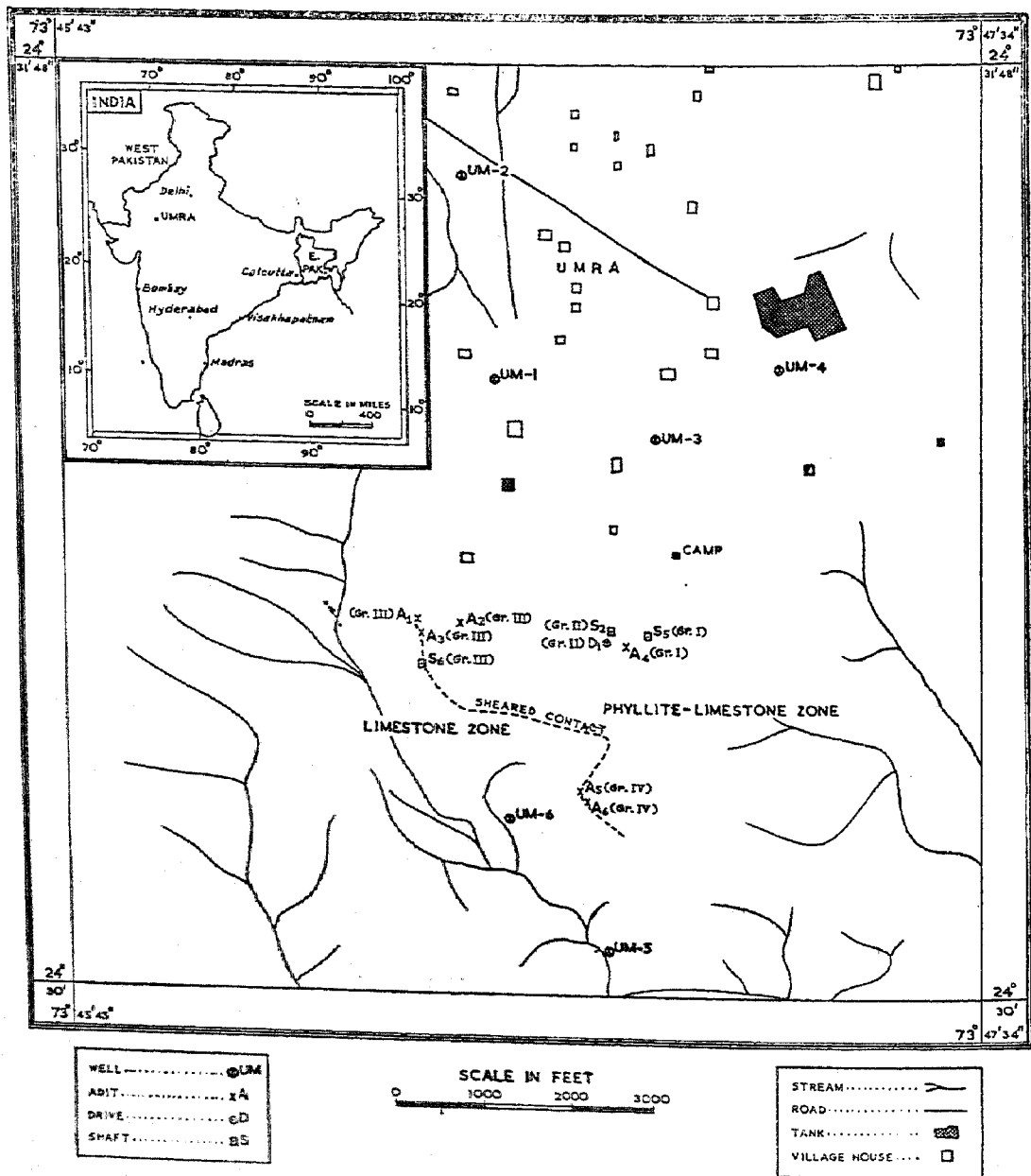


FIG. 1. Location Map.

CLIMATIC, HYDROLOGICAL AND CHEMICAL CONDITIONS

The area receives about 30 inches of rainfall and most of the precipitation takes place during the period June to September. The diurnal variation in temperatures may be of the order of 28° F. during most of the year (October to May). The average depth of the water table is about 50 feet. The pH of the waters is in the range of 7.5–9.0.

COLLECTION OF WATER SAMPLES

Ten water samples (1000 ml. each) were collected during December 1960 in duplicate in polyethylene bottles—six from the wells, three from the winzes in Adit No. III and one from Shaft No. II. The wells are in the phyllites-limestone zone. The locations of the water samples are shown in Fig. 1.

METHODS OF ANALYSIS

The samples are filtered and analysed for the following elements: Uranium, sodium, potassium, calcium, nickel, cobalt, copper and vanadium. The techniques of analysis employed are briefly described below:

Uranium.—The concentration of uranium is estimated with a fluorometer (Jarrel-Ash; Galvanek-Morrison type; mark V). The analytical technique is substantially the same as that described by Geier and Holland (1957).

Sodium, potassium and calcium.—These are determined with a flame-photometer (Kipp Model No. H 45) by the procedure described by Lillie Jenkins (1954).

Copper, cobalt, nickel and vanadium.—The concentrations of these elements are estimated spectrophotometrically (UNICAM instrument—spectra range 3500–8000 Å) by the methods of Sandell (1950, pp. 317, 283, 470–74, 609–11).

RESULTS

The analytical data are given in a consolidated form in Table I. The ranges of concentration of different elements in the waters are given below:

Uranium	..	2.6–49.6 ppb.	well-water;	1500–6000 ppb.	winze waters
Copper	..	$1.0-65.0 \times 10^{-5} \%$	(100–6500 ppb.)		
Cobalt	..	$1.0-16.5 \times 10^{-3} \%$	(10–165 ppb.)		
Sodium	..	3.1–27.2%			
Potassium	..	1.6–26.6%			
Calcium	..	1.7–14.2%			

TABLE I
Umra water samples, location and chemical data

S. No.	Sample No.	Location Long. E. and Lat. N.	Depth of water-table (for wells)	Concentration					
				U in ppb.	Cu %	Co %	Na %	K %	Ca %
1	UM-1	73° 46' 35½" 24° 31' 7"	30'-40'	3.4	8.0 × 10 ⁻⁵	1.0 × 10 ⁻⁶	27.2	26.6	n.d.
2	UM-2	73° 46' 32¾" 24° 31' 29"	60'-70'	19.1	5.0 × 10 ⁻⁵	1.0 × 10 ⁻⁶	3.1	2.3	3.1
3	UM-3	73° 46' 54" 24° 31' 3"	50'-60'	2.6	9.0 × 10 ⁻⁵	16.5 × 10 ⁻⁶	5.6	1.6	14.2
4	UM-4	73° 46' 8¾" 24° 31' 11"	60'	6.0	61.0 × 10 ⁻⁵	4.0 × 10 ⁻⁶	11.9	1.6	5.0
5	UM-5	73° 46' 47¼" 24° 30' 7"	50'	22.8	57.0 × 10 ⁻⁵	1.0 × 10 ⁻⁶	4.4	1.6	3.1
6	UM-6	73° 46' 38¼" 24° 30' 13"	50'	49.5	53.0 × 10 ⁻⁵	4.0 × 10 ⁻⁶	6.9	1.6	5.0
7	A ₃ W ₁	Adit No. III Winze No. I	..	1,554.5	1.0 × 10 ⁻⁵	..	24.4	4.4	5.9
8	A ₃ W ₂	Adit No. III Winze No. II	..	6,495.5	13.0 × 10 ⁻⁵	..	18.2	1.6	1.7
9	A ₃ W ₃	Adit No. III Winze No. III	..	5,455.5	5.5 × 10 ⁻⁵	8.0 × 10 ⁻⁶	17.5	1.6	1.3
10	S ₂	Shaft No. II	..	6,495.5	65.0 × 10 ⁻⁵	1.0 × 10 ⁻⁶	10.2	1.6	2.2

N.B.—UM-1 to UM-6 are well-waters; vanadium and nickel are absent in all samples.

Nickel is absent in waters, though its presence in trace quantities has been noted in the soil samples. Vanadium also is conspicuous by its absence in the waters, though the ores in the area are vanadiferous. The alkali contents of the waters are high.

DISCUSSION

The pattern of distribution of elements in the natural waters of the Umra area are discussed below element-wise.

Uranium.—A study of the field observation in the area brings out the following facts:—

1. Uranium and copper have distinctly separate mineralisation zones.
2. Uranium minerals are as a rule found surrounded by copper minerals but not *vice versa*.
3. Primary uraninite occurs along with its alteration products which form $\frac{1}{4}$ " to 1" thick veins of massive habit.

An analysis of the secondary geochemical dispersion pattern of uranium in the natural waters brings out the following features:

- (i) There is a marked difference in the uranium content of waters which come into contact with uranium mineralisation (winze waters) and those that move through ore-less rocks (Geochemical background in well waters—which in this area probably corresponds to the uranium in well water No. UM-3).
- (ii) The alkalinity of the waters, as indicated by high Na, K and Ca contents.
- (iii) The high pH values—varying from about 7.5 to 9.
- (iv) A considerable sulphide content (chalcopyrite and pyrite).
- (v) There does not seem to be any influence of the dissolved solids (of Na, K and Ca) on the uranium migration in the waters in this zone, as is evident from the absence of any relationship between these elements and uranium content.
- (vi) No correlation was observed between copper and uranium in water.

These features suggest that the uranium distribution pattern in waters at Umra apparently corresponds to the hydrogeochemical zonality of the non-bituminous type (Germanov *et al.*, 1958). The depth of the samples of waters fixes the zone as belonging to the transition zone between the upper

zone of weakly mineralised waters and the middle zone of more mineralised waters.

The following sequence of events might have resulted in the partitioning of uranium between the mobile aqueous phase and the immobile solid phase of the surficial environment:

1. Uranium mineralisation—formation of primary minerals of uranium (uraninite) with U^{+4} .
2. Copper mineralisation—formation of primary chalcopyrite.
3. Oxidation of U^{+4} into soluble $(U^{+6}O_2)^{+2}$ and the formation of secondary Cu-U ores like the insoluble torbernite and meta-torbernite.
4. Continued leaching by ground water of the primary uranium minerals resulting in the formation of uranium-bearing waters. The insoluble secondary Cu-U minerals could not have contributed to the Uranium in waters.

Copper.—The occurrence of copper in the area as primary sulphides (like chalcopyrite) and secondary carbonates (like malachite) and its presence in trace amount in waters could be traced for their source to the copper minerals associated with granitic intrusives.

The processes that result in the formation of malachite in the oxidation zone of limestone country are fairly well known. In the oxidation zone, the metal ions are freed from the sulphides with the formation of sulphates and sulphuric acid. The interaction of these acid solutions with limestones enhances the pH of the waters to the alkali side, resulting in the formation of free metallic ions of copper. The latter react with CO_2 -rich waters to form secondary copper minerals like malachite.

The copper-bearing waters in which copper is present, mostly as sulphate, pass through water-table to the zone of primary sulphides and bring about the secondary enrichment of primary sulphides, by precipitating sulphides of copper in that reducing environment. During the processes, some copper probably enters the waters in the form of colloidal suspension of basic carbonates (Yaakovleva, 1952). This accounts for the presence of traces of copper in waters, despite the fact that at high pH values of the level obtaining in the area, copper cannot remain in solution even though copper carbonates are sparingly soluble (copper precipitates at pH of 5.4–5.7). The absence of clear-cut differences between the copper content of winze and well waters may also be attributed to the process suggested by Yaakovleva (1952).

Vanadium.—The secondary uranium ores in the area are vanadiferous. The source of vanadium was probably the magnetite and ilmenite in the quartz veins in the country rocks. Vanadium is conspicuous by its absence in the waters and this observation could be explained in the light of its geochemistry.

Vanadium in magnetite and ilmenite is in the form of poorly soluble trivalent state. Under oxidising conditions and in an arid climate, vanadium is converted to soluble quinivalent state (Fisher and Stewart, 1961). "Under ordinary ground water conditions, the environment is reducing and alkaline but if atmospheric oxygen enters the system, it serves as a strong oxidising agent. The effect is to superpose a strongly oxidising environment over an essentially reducing environment. Under these conditions, V_2O_3 below the water table would probably remain insoluble indefinitely but, wherever it is raised to a place where it has free access to air, vanadium would continuously get oxidised into quinivalent state" (Garrels, 1953, 1955). The latter might have interacted with uranium, calcium and potassium to form the insoluble secondary minerals like carnotite and tyuyamunite, whose formation is favoured by the arid climate prevailing at Umra. The presence of vanadium in the secondary minerals and its absence in water is thus accounted for.

Cobalt.—Traces of cobalt found in waters are traceable to cobalt associated with copper and magnesium minerals. The distribution of cobalt in igneous rocks bears similarities to both copper and nickel. In the basic, intermediate and acid rocks the distribution of cobalt is actually closer to that of copper than to that of nickel. In the hydrothermal copper ore bodies of Belgian Congo and North Rhodesia, the dispersion pattern of cobalt tends to be more like copper than that of nickel (Wilson, 1953).

The presence of cobalt has been reported in a few waters but no cobalt was found in neutral or alkaline waters (Malyuga, 1949).

The processes that resulted in imparting some cobalt content to the waters in the area are visualised as follows:

In the oxidation zone under conditions of low pH, cobalt is leached by weakly acid waters. The high mobility of cobalt aids its transport downward (along with copper) to the water exchange zone. The rise in pH and dilution of weakly acid waters at the water exchange zone affect the mobility of cobalt, resulting in partial or complete precipitation. The observed low concentration of cobalt in most of the water samples and its absence in two can thus be accounted for.

Nickel.—Nickel could not be detected in waters of the area but paper-chromatographic analysis of soil leaches indicate the presence of the element in the soil samples. The nickel content of the soils might have been derived from the copper and iron sulphides (chalcopyrite and pyrite) with which nickel is associated.

Iron, nickel and cobalt which are characterised by close geochemical affinity in primary deposits, part ways later as a consequence of operation of supergene processes (Mason, 1958, p. 164). "Nickel does not form trivalent compounds but a dioxide is known, the formation of which even in alkaline solutions requires potentials somewhat higher than that for release of oxygen, from water" (Mason, 1958, p. 164). So, nickel neither goes into solution, nor does it get precipitated but it is 'scavenged' from waters and adsorbed on hydrated iron oxides. That this is indeed so, is supported by the frequent occurrence of nickel in hydrated iron and manganese ores (Krauskopf, 1956).

Health hazard.—Assuming that man's daily intake of water (in fluids) is 1500 ml. and his total body weight (inclusive of bones) is 70 kg., it is found that by drinking water from well No. 6 (with a uranium content of 50 ppb.), a man is exposed to a radiation dosage very much near the maximum permissible dosage for a population. So drinking water from well No. 6 may constitute a health hazard.

ACKNOWLEDGEMENTS

We wish to place on record our deep debt of gratitude to the late Prof. C. Mahadevan for his kind encouragement. The manuscript has been kindly reviewed by Dr. Lyman C. Huff of the United States Geological Survey and our colleague, Dr. C. Borreswara Rao. We are thankful to the Atomic Minerals Division of the Department of Atomic Energy for their kind permission to undertake this study in their mines. Mr. V. Chalapathi Rao of the Zoology Department has been of great help in spectrophotometric analysis. The financial assistance of the Council of Scientific and Industrial Research (India) is thankfully acknowledged.

REFERENCES

- Dar, K. K. and Nandi, H. .. *Proc. Int. Conf. on Peaceful Uses of Atomic Energy*, Geneva, 1958, 2, 696.
- Fisher, R. P. and Stewart, J. H. .. *Econ. Geol.*, 1961, 56, 509.
- Gsier, F. H. and Holland, W. H. .. *U.S.A.E.C. Bull. R.M.E.*, 1957, 1091, 5.
- Germanov, A. I., Batulin, S. G., Volkov, G. A., Lisitsin, A. K. and Serebrenikov, V. S. .. *Proc. Int. Conf. on Peaceful Uses of Atomic Energy*, Geneva, 1958, 2, 161.

- Garrels, R. M. .. *Amer. Min.*, 1953, 38, 1251.
.. *Ibid.*, 1955, 40, 1004.
- Krauskopf, Konrad .. *Geochim et Cosmochim acta*, 1956, 9, 1.
- Lillie Jenkins .. *Tech. Report of U.S. Geol. Surv. T.E.I.*, 1954, 453, 4.
- Malyuga, D. P. .. *Dokl. Akad. Nauk., S.S.S.R.*, 1949, 67, 1057.
- Mason, B. .. *Principles of Geochemistry*, John Wiley, New York, 1958.
- Sandell, E. B. .. *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1950.
- Wilson, H. D. B. .. *Econ. Geol.*, 1953, 48, 370.
- Yaakovleva, M. N. .. *Byull. Moskov. Obschestva, Ispytatel Prirody, Otdel, Geol.*, 1952, 27 (6), 3-21.