

closure of graphite in between (Fig. 3) and by their different optical orientation. (Rast, 1965).

The growth stage III is separated from the growth stage II by the presence of a second graphite closure in between them (Figs. 1 and 3).

The orientation of the graphite in Fig. 3, however, suggests that the growths in these directions are rapid and the inclusions are the relics imprisoned within the dendrites (Rast, 1965). The dendritic growth is followed by the layeritic growth marked by the orientation of the graphite layer (Fig. 3). This indicates the decrease of the supersaturation limit of the constituent materials from the dendritic growth to the layeritic growth.

Growth-deformation relation: The growth stage III incorporates the S_1 schistosity (Fig. 5) marked by the compositional variation of the graphite layer and the axial plane schistosity S_2 marked by the orientation of the mica flakes (Fig. 5).

Initially S_1 & S_2 represent an angular relationship between themselves within the staurolite porphyroblasts (Fig. 5); but with the intensification of the deformation S_2 plane became acutely folded (Fig. 4) and the S_2 plane became parallel to the S_1 plane. The evidence of rotation of the porphyroblast as a whole has been noticed from the high angle relationship between S_1 and S_2 (Ghosh, 1963).

Conclusion: From the study of the inclusions within the staurolite, it may be concluded that the crystal started nucleating in an essentially static condition, and the growth stages I & II of the crystal coincide with the static condition while the growth stage III outlasted the deformation that produced the S_1 and S_2 schistosity of the area.

Acknowledgements: The work was carried out in the Department of Geological Sciences, Jadavpur University, under the constant guidance of Dr. P. S. Chakraborty. The author is indebted to Prof. S. Deb, for his interest in this problem and to Dr. A. K. Saha for critically reading the manuscript and for his suggestions for improvement. He is grateful to the Director-General of C.S.I.R. for financing the scheme and to the Director-General of G.S.I., for giving all facilities during field work. Thanks are also due to the Director of C.G.C.R.I. for his kind help from his laboratory and to Sri N. Bhaumik for his hospitality and advice.

REFERENCES

- GHOSH, SUBIR KUMAR, (1963) Structural, metamorphic and migmatitic history of the area around Kuilapal, Eastern India. *Q.J.G.M.M.S.I.* v. 35, No. 4.
- RAST, NICHOLAS (1965) Nucleation & growth of metamorphic minerals—control of metamorphism edited by Pitcher & Flinn.

A NOTE ON THE GEOCHEMISTRY OF VANADIUM AT UMRA, RAJASTHAN

V. V. S. S. TILAK

Department of Geology, Andhra University, Waltair

With the object of delineating the primary and secondary geochemical dispersion patterns in the rocks, soils and waters in the uranium prospect at Umra, Rajasthan, the concentration of vanadium has been determined by spectrophotometer (Unicam SP 600 with a spectral range of 3500–8000 Å) along with other elements like U, Cu, Co, Ni, etc. adapting the procedures given by Sandell (1950).

Vanadium is conspicuous by its absence in the waters, and is present in the rocks and soils of the area. The concentration of vanadium in the rocks varies from 25 ppm to as high as 4000 ppm with a mean value of 980 ppm, whereas in soils its concentration varies from 850 to 2600 ppm with a mean value of 1102 ppm. The general level of concentration of vanadium in the soils is higher in comparison with that in rocks. Its distribution in rocks as well as in soils is unimodal, positively skewed. In the different types of rocks that were analysed, vanadium seems to be concentrated at comparable levels in limestones and phyllites (average concentration in limestones—1186 ppm and phyllites and schists—1014 ppm). The concentration is least in the shales (Table I).

TABLE I
CONCENTRATION OF VANADIUM IN ROCKS AND SOILS

Name	Number of samples analysed	Range in ppm	Average in ppm
Limestones	9	250 - 3700	1186
Shales & slaty shales	7	25 - 1200	625
Crushed rock	3	375 - 1650	808
Phyllites & schists	19	150 - 4000	1014
Soils	34	850 - 2600	1099

Discussion: The source of vanadium in the rocks and soils of the area could probably be traced to the magnetite and ilmenite in the quartz veins that are present in the country rocks. It is quite likely that chlorite, biotite and other silicate minerals might have also contributed to its concentration both in rocks and soils. (Fischer & Stewart, 1961; McKelvy, Everhart & Carrels, 1955 p. 493; McLaughlin, 1955). Its total absence in the waters of the area and its presence in the rocks and soils only in such high concentration indicates that it must be present in its insoluble tri- or tetravalent form (in which state it is highly immobile). The conditions of its oxidation to pentavalent form have been discussed by Garrels (1953; 1955).

An analysis of the data in respect of trace element constitution of the rocks and soils shows that despite there being an appreciable quantity of vanadium in the area, almost all the secondary uranium minerals are phosphates (autunite, torbernite, saleite etc.) with a few hydroxides like gummite. This would mean that uranium in the area has tended to form with other elements like Ca, Mg, Cu etc., in preference to its forming vanadates. This feature may be attributed to the readily available pentavalent phosphates in the black shales of the area. Further, phosphorus occurs in nature only in the pentavalent oxide form as phosphate ion $(PO_4)^{3-}$ and hence its precipitation does not depend on oxidation potential (Eh) of the surrounding medium (Ronov and Korzina, 1960, p. 809). Even if phosphorus were present in the lower valent state, it readily gets oxidised to pentavalent P_2O_5 . Under the conditions of Eh and pH obtaining in the area (estimated Eh) P_2O_5 tends to combine with soluble uranyl ions and other available metallic ions of Ca, Mg and Cu to form phosphates.

The behaviour of vanadium even under identical conditions of Eh and pH differs depending on the nature, concentration and ionic state of the associated elements. Magnetite, ilmenite and to some extent chlorite and biotite release vanadium on weathering in its tri- or tetravalent (insoluble) form which cannot be converted into pentavalent (soluble) state thereby leading to the production of soluble vanadyl ions to form uranyl vanadates like carnotite and tyuyamunite. Garrels (1953, p. 1264) discusses the stability relations of vanadium oxides under natural conditions and points out that the trivalent vanadium oxide (V_2O_3) or its hydrate is its lowest valent vanadium that would get oxidised to next higher valent form (tetravalent oxide) at about the same potential necessary, which would convert a sulphide to sulphate. This would result in V_2O_3 coexisting in equilibrium with various metal sulphides such as pyrite and galena. The quadrivalent vanadium probably oxidises through a complex series of V(IV) and V(V) oxides.

It is therefore suggested that though vanadium is present in sufficient quantity in the area (Table I), it is not available in a soluble form which alone could lead to the formation of vanadates. Hostetler and Garrels (1962) point out that the 'carnotite stability' is very sensitive to changes in ionic activity rather than Eh and pH (except for distinctively reducing conditions), and its precipitation is critically controlled by amounts of uranium, vanadium and CO_2 in solution. Therefore the formation of uraniferous phosphate in this area in preference to vanadates is apparently controlled not only by Eh factor but also by the ionic activity of the associated elements.

The author is grateful to Prof. U. Aswathanarayana for his interest in the work. The Atomic Minerals Division of the Department of Atomic Energy gave him permission to undertake the study in their mines.

REFERENCES

- FISCHER, R. P. and STEWART, J. H., (1961) Copper, vanadium and uranium deposits in sandstone—their distribution and geochemical cycles. *Eco. Geol.*, v. 56, pp. 509-520.
- GARRELS, R. M., (1953) Some thermodynamic relations among the vanadium oxides and their relation to the oxidation state of uranium ores of the Colorado plateau. *Am., Min.*, v. 38, pp. 1251-1265,
- (1955) Relation of vanadium and uranium oxide stability fields. *Am., Min.*, v. 40, pp. 1004-1020.
- HOSTETLER, P. B. and GARRELS, R. M., (1962) Transportation and precipitation of uranium and vanadium at low temperatures with special reference to sandstone type uranium deposits. *Eco. Geol.*, v. 57, No. 2, pp. 137-167.
- MCLAUGHLIN, R. J. W., (1955) Geochemical changes due to weathering under varying conditions. *Geochim. et Cosmochim. Acta*, v. 8, pp. 109-130.
- McKELVY, V. E., EVERHART, D. L. and GARRELS, R. M., (1955) Origin of uranium deposits. *Eco. Geol.*, 50th Ann. Vol. Pt. 1, pp. 464-533.
- RONOV, A. B. and KORZINA, G. A., (1960) Phosphorous in sedimentary rocks. *Geochemistry*, v. 8, pp. 805-829.
- SANDELL, E. B., (1950) *Colorimetric determination of traces of metals*. Interscience, New York.