Chemical Geology, 14 (1974) 23—30

URANIUM AND THORIUM IN POTASH-RICH RHYOLITES FROM WESTERN BAHIA (BRAZIL)

G. PAOLO SIGHINOLFI* and TEREZA SAKAI

Institute of Geosciences and Institute of Physics, Federal University of Bahia, Salvador, Bahia (Brazil)

(Received April 12, 1974; revised and accepted August 20, 1974)

ABSTRACT

Sighinolfi, G.P. and Sakai, T., 1974. Uranium and thorium in potash-rich rhyolites from western Bahia (Brazil). Chem. Geol., 14: 23—30.

The U and Th distribution in K-rich acid metavolcanics affected by postmagmatic processes has been studied. Th (20 ppm) and U (2.41 ppm) average abundances are well within the normal ranges for granitic rocks, but the Th/U values are appreciably higher than most of the values reported. Since the rhyolitic magma is supposed to have been formed by partial melting of pre-existing rocks, the high Th/U ratios may be due: (1) to an extreme magmatic fractionation towards a K-rich trend in the magma chamber or during magma displacement; and (2) to high Th/U ratios in the original material, probably ancient crystalline basemental rocks depleted in U with respect to Th during previous cycles. The possible influence of postmagmatic processes on U and Th distribution is discussed, and evidence of U mobilization and redistribution within the formation is set forth.

INTRODUCTION

Sighinolfi and Conceção (1974) recently studied the petrology and chemistry of potash-rich extrusives, slightly metamorphosed under greenschist facies conditions, occurring in an ancient Precambrian metasedimentary sequence in the western Bahia State (Brazil). One of the main points of interest was their peculiar chemical composition, for they are abnormally rich in potash and sometimes silica, while being almost completely lacking in elements like Ca, Mg and Sr. In addition, complex, and as yet unidentified, postmagmatic processes (metasomatic-hydrothermal) have induced marked changes in the main mineralogy of the rocks. In the absence of adequate data regarding the general geology and tectonics of the area, these facts, and, in particular, the discrepancies observed in the formation setting relative to the surrounding metasediments, have raised doubts as to the volcanic history and postmagmatic evolution of these extrusives.

Through a study of the uranium and thorium distribution in these rocks

*Present address: Istituto di Mineralogia, Università di Modena, Italy

the present paper sets out not only to contribute to our scant store of knowledge concerning these elements in acid volcanics, but also to clarify the origin and evolution of the rocks themselves.

SUMMARY OF GEOLOGY, CHEMISTRY AND GENETICAL INTERPRETATIONS

Volcanics of rhyolitic and rhyo-dacitic composition (Froes et al., 1972; Sighinolfi and Conceção, 1974) are localized in the Ibitiara-Ibiajara area, (western Bahia State); they belong to a stable unit consisting mainly of ancient Precambrian basemental rocks covered, for the most part, by a younger sedimentary sequence (arenites, phillites, slates) metamorphosed under greenschist-facies conditions. The extrusives form a belt extending approximately 60 km NW—SE, 8—10 km wide following the main tectonics and structure of the area, in particular that of the metasediments. Nevertheless, discordant contacts between the volcanics and sediments in some parts were also noted. Age data based only on a few determinations (Tavora et al., 1967) give about 1 billion years (Upper Precambrian) for the metasediments and 390 million years for the volcanic rocks. Foliation, scistosity and tectonization, which are practically absent in the centre of the formation, increase towards its edges. Unaltered or only slightly altered samples consist of quartz and K-felspar phenocrysts immersed in a microcrystalline iron oxide-rich matrix. Postmagmatic processes (metasomatism) have induced strong sericitization and microlinitization which is generally diffuse but much more intense at the periphery of the formation, where metasomatism leads locally to K concentrations. Later hydrothermal activity was responsible for the formation of abundant quartz veins. Chemical analysis revealed an unusually high K content, which causes the rocks to resemble shoshonitic types, low Ca, Mg and Sr contents and very high Rb/Sr ratios. Some hypotheses regarding the origin of these unusual rocks have been put forward: (1) the formation and extrusion of a magma of granitic composition, rather rich in potassium, later metamorphism inducing intense K-mobilizations which in some parts forced the rocks to develop towards the present composition; (2) extreme magmatic fractionation towards K-rich trends in the magma chamber or during magma displacement; (3) pyroclastic origin of most of the material and later intense remobilizations during metamorphism. Whatever the type of extrusion mechanism, the magma is considered to derive from partial melting of K-rich material of the basement or of superimposed formations. Finally, this volcanism could be related to internal adjustments along old lines of weakness, since it seems to have occurred approximately at the contacts between two stable units (São Francisco craton and Salvador craton, according to Cordani, 1973) which could have drawn close to or collided with each other following general trends of the continental tectonics.

ANALYTICAL METHODS

Uranium and thorium were determined by gamma-ray spectrometry, using a 1024-multichannel analyzer (5401 B Hewlett-Packard mod.) connected to a 10 cm × 8 cm NaI (Tl) crystal. This crystal was associated with a photomultiplier with quartz window. Using 800 g of crushed rock sample, Th was determined from the 208 Tl peak (2.62 MeV); U from 214 Bi peak (0.607 MeV), after subtraction of the 208 Tl contribution by the tangent method. The calibrations used were made by Nordemann (1966) on a similar equipment using identical crystal and geometry of detection. The maximum error is estimated to be about 10% for Th and 20% for U.

DISCUSSION OF THE RESULTS

Table I reports the Th and U content together with potassium data taken from Sighinolfi and Conceção (1974) for 29 samples of acid extrusives. The samples were divided into two groups, taking into account the rate of post-magmatic transformation suffered. The average contents of Th (20 ppm) and U (2.41 ppm), derived from the sum of all the samples, fall within normal limits for granitic rocks, although the U values are at the lower end of the scale (Table II). For this reason the Th/U ratios are notably higher than those reported in the literature for granitic suites (see the review of Rogers and Adams, 1969). Acid rocks known to present high Th/U ratios are medium- to high-grade metamorphic rocks (gneisses, granulites) from various ancient crystalline basemental areas (see e.g. Lambert and Heier, 1967; Narayanaswamy and Venkatasubramaniam, 1969; Heier and Thoresen, 1971) and sometimes also rhyolitic extrusives (Ewart and Stipp, 1968). The variation coefficents (*C*) for

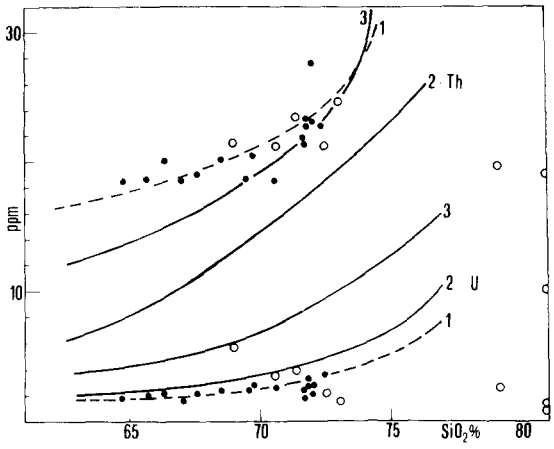

Fig.1. Thorium and uranium versus silica in the Bahia extrusives (1) and in two American igneous acid suites (2 = Valles Mountains, 3 = Big Bend National Park). Solid circles indicate unaltered samples, open circles altered samples. (After Rogers and Adams, 1969.)

TABLE I

Uranium, thorium and potassium in acid extrusives from western Bahia

Sample	Th	U	Th/U	K_2O
Unaltered or slightly altered samples				
GIB 4	18.6	1.94	9.6	4.12
GIB 7	23.2	3.20	7.2	5.27
GIB 9	21.7	2.54	8.5	5.70
GIB 11	23.0	2.66	8.6	5.35
GIB 14	18.7	2.14	8.7	3.95
GIB 17	21.4	1.68	12.7	6.18
GIB 18	18.6	2.51	7.4	5.07
GIB 21	20.2	2.42	8.3	3.69
GIB 27	22.8	2.81	8.1	5.35
GIB 30	20.5	2.80	7.3	4.56
GIB 31	18.5	2.50	7.4	4.95
GIB 34	19.1	2.20	8.7	4.20
GIB 36	18.2	2.59	7.0	
GIB 38	27.6	2.00	13.8	4.59
GIB 43	22.1	2.64	8.4	
GIB 47	18.5	1.46	12.7	3.62
GIB 49	22.7	3.57	6.3	4.72
Average (18 sampl.)	20.9	2.43	8.9	
C%	11.5	21.2		
Strongly altered samples				
GIB 10	19.0	1.07	17.7	3.71
GIB 19	10.0	0.95	10.5	1.88
GIB 22	19.5	2.48	7.9	3.63
GIB 23	23.4	3.95	5.9	6.37
GIB 24	21.5	5.70	3.8	4.47
GIB 26	15.4	3.16	4.9	
GIB 28	17.0	0.60	28.3	
GIB 41	21.2	2.07	10.2	4.68
GIB 42	24.5	1.52	16.1	7.29
GIB 44	21.1	3.65	5.8	6.32
GIB 45	12.8	0.91	14.1	
Average (11 sampl.)	18.7	2.37	11.4	
C%	24.0	65.4		
Total average (28 sampl.)	20.0	2.41	9.8	
C% (total samples)	17.3	41.9		

C% = relative standard deviation

TABLE II

Uranium, thorium and Th/U ratio in acid rocks and in other correlated materials

	U(ppm)	Th(ppm)	Th/U	Reference
Extrusives, western Bahia (averages)	2.41	20.0	9.8	this paper
Concentration ranges in granitoids	2.2—15 (19 suites)	8—56 (16 suites)	3.7—6.3 (15 suites)	from the compilation of Rogers and Adams (1969)
Ave. granitic rocks	4.8	17	3.54	Taylor (1966)
Rhyolite lavas, New Zealand (averages)	2.64	11.5	4.32	Ewart and Stipp (1968)
Rhyolite ignimbrites, New Zealand (ave.)	2.48	11.4	4.62	Ewart and Stipp (1968)
Rhyolites and dacites, western U.S.A. (ave.)	5.0			Coats (1956)
K-rich syenites, Switzerland (ave.)	22.1	66.0	3.19	Labhart and Rybach (1971)
Gneisses, India (concentration ranges)	0.8—9.4	12.7—55.6	5.1—14.6	Narayanaswamy and Venkatasubramaniam (1969)
Amphib. facies-horn. gran. subfacies rocks (averages)	2.0	17.5		Lambert and Heier (1967)

Th and U are much higher in the severely-altered than in the unaltered samples, particularly owing to the strong spreading of some samples, as occurs for potassium. Thus, postmagmatic processes seem to be responsible for such occasional spreadings, even if a certain heterogeneity due to contaminations by foreign material cannot be excluded, because maximum alteration occurs in the outer part of the formation.

Correlations have been sought between Th and U content and other rock components. The plot of Th and U against silica (Fig.1) exhibits the normal magmatic trend, i.e. the Th/U ratio increasing with differentiation (Ragland et al., 1967; Rogers and Adams, 1969; Dawson and Gale, 1970), for although both thorium and uranium increase with silica, Th does so more than U. No sympathetic variation has been noted between the Th/U ratio and potassium (Fig.2a) or the orthoclase-plagioclase ratio, as is sometimes found (Rogers and Ragland, 1961; Heier and Rogers 1963; Ewart and Stipp, 1968).

IMPLICATIONS AS REGARDS VOLCANIC HISTORY AND POSTMAGMATIC PROCESSES

Volcanic history

The plot of the Th/U ratio versus U content (Fig.2b) shows that Th/U ratios are strictly dependent on the U content. Neither Th nor U vary much in the unaltered samples, thus suggesting that their actual distribution repre-

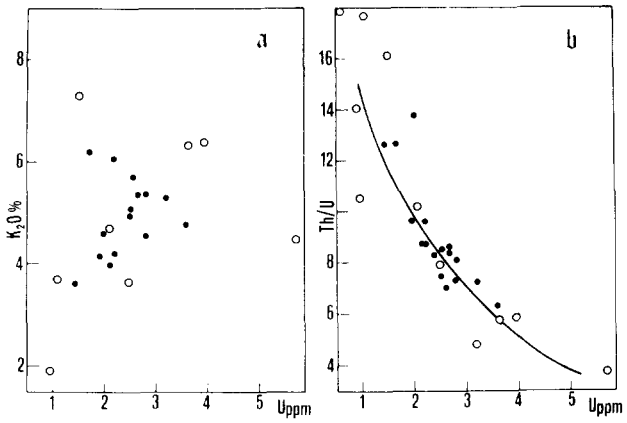

Fig.2. Diagrams of (a) K_2O versus U, and (b) ratio Th/U versus U.

sents an original feature of the magma. In order to explain the high Th/U ratios found therefore, two main hypotheses must be considered:

(1) Extreme fractionation of a granitic magma occurred in the magmatic chamber and/or during displacement of the magma. Partial separation between U and Th may have occurred in the final stages owing to varying oxidative conditions. The unusual potassium concentration may have been caused by the intervention of a volatile transfer-like mechanism as suggested by Ewart et al. (1968), although in this case a major concentration of highly charged elements, including Th and U, would be expected.

(2) Partial melting of K-rich material characterized by high Th/U ratios caused by previous depletions of U with respect to Th. In this case, the K-rich character of the magma is consistent with the melting of markedly biotite-rich materials according to the model proposed by Waters (1955) and Thorpe (1971). Thus, this volcanism may have correlated with a recycling episode of ancient basemental rocks, already previously depleted in U with respect to Th through repeated partial meltings, in accordance with current evolutionary models of the earth's crust (Shaw, 1968; Sighinolfi, 1969, 1971). Moreover, the possibility that fusion might involve more recent material (sediments), as already suggested for the genesis of other acid extrusives in continental areas (see e.g. Ewart and Stipp, 1968), cannot be excluded.

U and Th distribution and postmagmatic processes

The stronger variations of Th and U, but especially of the latter, in the altered samples show how these elements were involved in the secondary processes to which the rocks were submitted. Few studies have been directed towards an understanding of the behaviour of Th and U during hydrothermal or metasomatic reactions. The tendency of uranium to be oxidized to the soluble uranyl ions permits U to be mobilized easily in superficial processes.

This leads to the assumption that uranium is also deeply involved in hydrothermal or metasomatic activity, while thorium would be relatively immobile, as vouched for by its concentration in residual material such as soil. The redistribution of uranium (that of thorium seems to have been negligible) could have occurred during K-metasomatism to give microlinitization and sericitization; however, the lack of any K—U correlation (Fig.2a) shows that it did not follow the pattern of potassium. U migration may have occurred either in the same fluid phase accompanying metasomatism or during later hydrothermalism, for example through groundwater leaching as suggested by Rosholt et al. (1971). Hydrothermal fluids of low temperature (100—250° C), though weak, have been found (Brimhall and Adams, 1969) to cause effective redistribution of elements like U. In our case, the fluids, besides being alkaline of course, must be oxidative to form soluble uranyl ions. Scattered reprecipitation of uranium may have occurred where the oxidative conditions were locally lowered, that is, according to Barbier and Ranchin (1969), where the chemical alteration effects are weak. Here, the uranium so released precipitates as autunite along cracks. Thus the anomalous U concentration in some samples can be interpreted (Labhart and Rybach, 1971) as possible signs of postmagmatic remobilizations.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Daniel Nordemann who provided instruction and suggestions in carrying out analysis and Prof. Teresa Cardoso for helpful assistance in collecting samples. Financial support for this research was provided by Brazilian CNPq and PLAN-FAB.

REFERENCES

Barbier, J. and Ranchin, G., 1969. Influence de l'altération météorique sur l'uranium à l'état de traces dans le granite à deux micas de St. Sylvestre. Geochim. Cosmochim. Acta, 33: 39—47

Brimhall, W.H. and Adams, J.A.S., 1969. Concentration changes of thorium, uranium and other metals in hydrothermally altered Conway granite, New Hampshire. Geochim. Cosmochim. Acta, 33: 1308—1311

Coats, R.R., 1956. Uranium and certain other trace elements in felsic volcanic rocks of Cenozoic Age in Western United States. U.S. Geol. Surv. Prof. Paper, 300: 75—88

Cordani, U.G., 1973. Evolução geológica pré-cambriana da faixa costeira do Brasil, entre Salvador e Vitória. Livre Docência Thesis, Universidade de São Paulo

Dawson, J.B. and Gale, N.H., 1970. Uranium and thorium in alkalic rocks from the active carbonatite volcano Oldoinyo Lengai (Tanzania). Chem. Geol., 6: 221—231

Ewart, A. and Stipp, J.J., 1968. Petrogenesis of the volcanic rocks of the central North Island, New Zealand, as indicated by a study of $^{87}Sr/^{86}Sr$ ratios, and Sr, Rb, K, U and Th abundances. Geochim. Cosmochim. Acta, 32: 699—736

Ewart, A., Taylor, S.R. and Capp, A., 1968. Geochemistry of pantellerites of Mayor Island, New Zealand. Contrib. Mineral. Petrol., 17: 116—140

Froes, R.I.B., Dultra, E.T., Sampaio Filho, H.A. and Oliveira, M.A.F.T., 1972. Petrologia comparada das rochas efusivas da Chapada Diamantina, BA. XXVI Congr. Bras. Geol., Boll. No.1, Belem

Heier, K.S. and Rogers, J.J.W., 1963. Radiometric determination of thorium, uranium, and potassium in basalts and in two magmatic differentiation series. Geochim. Cosmochim. Acta, 27: 137—154

Heier, K.S. and Thoresen, K., 1971. Geochemistry of high-grade metamorphic rocks, Lofoten-Vesterålen, North Norway. Geochim. Cosmochim. Acta, 35: 89—99

Labhart, T.P. and Rybach, L., 1971. Abundance and distribution of uranium and thorium in the syenite of Piz Giuv (Aar-massif, Switzerland) Chem. Geol., 7: 237—251

Lambert, I.B. and Heier, K.S., 1967. The vertical distribution of uranium, thorium and potassium in the continental crust. Geochim. Cosmochim. Acta, 31: 377—390

Narayanaswamy, R. and Venkatasubramaniam, V.S., 1969. Uranium and thorium contents of coexisting gneisses, granites and pegmatites. Geochim. Cosmochim. Acta, 33: 1007—1009

Nordemann, D., 1966. Emissions gamma de quelques météorites et roches terrestres, évaluation de la radioactivité du soil lunaire. Thesis, Université de Paris

Ragland, P.C., Billings, G.K. and Adams, J.A.S., 1967. Chemical fractionation and its relationship to the distribution of thorium and uranium in a zoned granite batholith. Geochim. Cosmochim. Acta, 31: 17—33

Rogers, J.J.W. and Adams, J.A.S., 1969. Thorium. In: Handbook of Geochemistry. Springer-Verlag, Berlin

Rogers, J.J.W. and Ragland, P.C., 1961. Variation of thorium and uranium in selected granitic rocks. Geochim. Cosmochim. Acta, 25: 99—109

Rosholt, J.N., Prijana and Noble, D.C., 1971. Mobility of uranium and thorium in glassy and crystallized silicic volcanic rocks. Econ. Geol., 66: 1061—1069

Shaw, D.M., 1968. A review of K—Rb fractionation trends by covariance analysis. Geochim. Cosmochim. Acta, 32: 573—601

Sighinolfi, G.P., 1969. K/Rb ratio in high-grade metamorphism: a confirmation of the hypothesis of a continual crustal evolution. Contrib. Mineral. Petrol., 21: 346—356

Sighinolfi, G.P., 1971. Investigations into deep crustal levels: fractionating effects and geochemical trends related to high-grade metamorphism. Geochim. Cosmochim. Acta, 35: 1005—1021

Sighinolfi, G.P. and Conceção, M.T.L., 1974. Petrologia e Geoquimica de riolitos alcalinos pre-cambrianos de Oeste da Bahia. XXVIII Congr. Bras. Geol., Boll. No.1, Porto Alegre

Tavora, F.J., Cordani, U.G. and Kawashita, K., 1967. Determinações de idade—potássio—argónio em rochas da região central da Bahia. Anais XXI Congr. Bras. Geol., pp.234—244

Taylor, S.R., 1966. The application of trace element data to problems in petrology. In: L.H. Ahrens, F. Press, S.K. Runcorn and H.C. Urey (Editors), Physics and Chemistry of the Earth. Pergamon Press, Oxford, 6: 133—213

Thorpe, R.S., 1971. A potash-rich trachyte from the Precambrian of England. Contrib. Mineral. Petrol., 31: 115—120

Waters, A.C., 1955. Volcanic rocks and the tectonic cycle. Geol. Soc. Am., Spec. Paper, 62: 703—722