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Thallium in deep-seated crustal rocks

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Abstract—A Precambrian granulite terrain of the Brazilian shield presents an average Tl content of 350 ppb, very near to Shaw's figure for the lower continental crust. Thallium, as in other rock types, shows close coherence with Rb and K. The mean Rb/Tl value (193 for 53 samples) falls in the range of the 'normal' crustal values, while the K/Tl values (145,000 average) are higher than values for igneous rocks, as are the values for K/Rb. The results support the authors' hypothesis that granulitic rocks have undergone partial melting with contemporaneous depletion of Rb and Tl in relation to K.

INTRODUCTION

VERY SCANTY data are available on thallium distribution in metamorphic formations, particularly in high-grade metamorphic rocks and nothing is known about thallium behaviour in sequences of increasing grade of metamorphism. Conclusions of some investigations (see the review by DE ALBUQUERQUE and SHAW, 1972) show that the thallium content of various metamorphic rocks depends mainly on the mineralogical composition, and that granulitic rocks may be depleted in thallium in relation to other rocks. Granulites are normally considered (see SHAW, 1972) as deep-seated crustal materials, and therefore trends followed by elements in granulites may be considered representative trends of the lower continental crust. The present paper describes thallium behaviour in a granulite terrain in the Precambrian Brazilian shield on which a number of chemical studies have already been published (SIGHINOLFI, 1970, 1971, 1972).

Thallium was determined in 62 samples by flameless A.A. spectroscopy using the Perkin–Elmer heated graphite atomizer HGA-70 and Model 303 spectrophotometer. Thallium was previously extracted in an ether phase following the procedure used by FRATTA (1973). The detailed method here used is described by SIGHINOLFI (1973). Sample aliquots of 0·2 g were used and the detection limit can be placed at about 20 ppb. Precision of the bulk analysis depends on the Tl levels in the sample. In the range 20–50 ppb an error of 30–50 per cent must be considered; for Tl content above 50 ppb, precision becomes good (error <10 per cent).

Accuracy checks were carried out on USGS standard rocks. Duplicate determinations on each standard give the following values (ppb): W-1 105–110, G-2 950–1180, AGV-1 535–590, GSP-1 1520–1550 and BCR-1 280–300.

ANALYTICAL RESULTS

Table 1 reports thallium data and includes values of the Rb/Tl and K/Tl ratios. Eight samples are characterized by Tl levels below the detection limit (20 ppb) and in computing the average Tl value, they were arbitrarily considered to contain

Table 1. Thallium content and Rb/Tl and K/Tl values

Sample	Tl (ppb)	Rb/Tl	K/ Tl × 1000	Sample	Tl (ppb)	Rb/Tl	K/ Tl × 1000
Il 1	<20	—	—	Il 47	150	507	207
Il 6	30	300	123	Il 50	990	124	40
Il 7	20	250	155	Il 52	270	341	158
Il 8	120	142	77	Il 53	<20	—	—
Il 9	270	130	78	Il 54	100	830	362
Il 10	70	814	366	Il 55	>10000	—	—
Il 12	120	108	67	Il 56	220	114	84
Il 14	20	280	120	Il 57	940	97	39
Il 17	40	140	70	Il 58	1620	116	23
Il 18	940	87	32	Il 59	520	104	40
Il 19	30	253	160	Il 60	<20	—	—
Il 24	640	91	39	Il 61	<20	—	—
Il 25	50	200	122	Il 62	130	223	145
Il 26	180	139	83	Il 63	40	225	175
Il 27	110	118	111	Il 64	40	250	122
Il 28	40	150	145	Il 66	<20	—	—
Il 29	<20	—	—	Il 67	<20	—	—
Il 30	<20	—	—	Il 68	280	179	90
Il 31	415	106	47	Il 69	220	159	95
Il 32	970	114	30	Il 70	290	148	57
Il 33	480	108	30	Il 71	140	143	99
Il 34	2640	80	21	Il 72	200	210	72
Il 36	80	462	275	Il 73	360	167	63
Il 38	350	97	70	Il 74	480	119	42
Il 39	530	149	57	Il 76	30	233	333
Il 40	990	93	23	Il 77	1140	91	32
Il 41	790	115	36	Il 78	120	83	58
Il 42	1410	83	28	Il 79	320	87	62
Il 43	80	187	102	Il 82	70	143	194
Il 44	190	226	135	Il 83	390	87	57
Il 45	380	216	68	Mean	350*	193†	145†
Il 46	250	228	108				

* Number of samples = 61 (see text).
† Number of samples = 53.

10 ppb Tl. This procedure cannot influence sensibly the calculated thallium average for the whole terrain, and these eight samples were not considered in computing the averages for Rb/Tl and K/Tl ratios.

Sample Il 55, characterized by a very high Tl content (more than 10 ppm), was also excluded from all the calculations, in order not to falsify the figures for the whole terrain. This assumption is justified because this thallium anomaly seems to be due to a localized process which later affected the terrain. In fact, sample Il 55, even if mineralogically true granulite, has an abnormally high microcline content, sometimes concentrated in the form of recrystallized veins, and later hydrothermally deposited K-felspar (particularly of amazonitic variety) is known to be very rich in thallium (SITNIN, 1960).

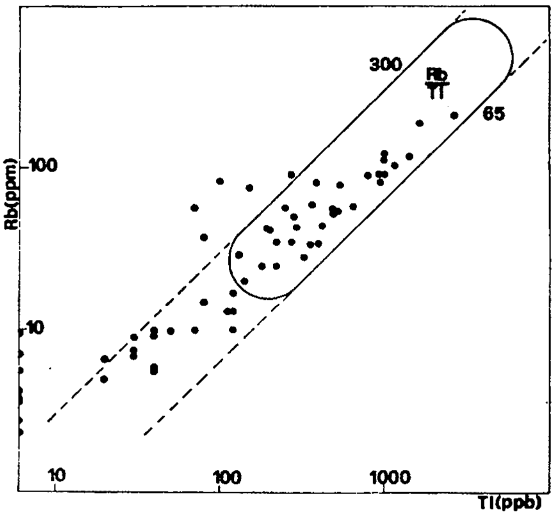

Fig. 1. Rb–Tl relationship. Area between dashed lines: terrestrial Rb/Tl values. Area outlined: composition ranges for igneous rocks (from DE ALBUQUERQUE and SHAW, 1972).

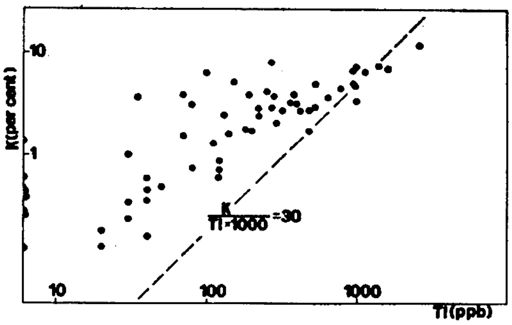

Fig. 2. K–Tl relationship. K/Tl × 1000 = 30: average value for igneous rocks (DE ALBUQUERQUE and SHAW, 1972).

Tl–Rb–K RELATIONSHIPS AND IMPLICATIONS ON DEEP CRUSTAL PROCESSES

The geochemistry of thallium in the granulites analysed, as in igneous rocks, is dominated by the close coherence with rubidium and potassium (Figs. 1 and 2). The average thallium content in the whole terrain (350 ppb) agrees with the figure, deduced by extrapolations by SHAW (1972), for the lower continental crust (400 ppb). The Rb/Tl values fall for the most part within the range of 'igneous' values (Fig. 1) and the mean value (193) is slightly higher than the average for igneous rocks (about 150, following DE ALBUQUERQUE and SHAW, 1972). The K/Tl values, on the contrary, are markedly higher than most 'igneous' values, and the mean value is two or three times greater than some proposed averages for both igneous rocks and oceanic tholeiites (see Table 3). From the data of Table 2, thallium appears to be more strongly correlated with rubidium than with potassium. Furthermore,

Table 2. Correlation coefficients and some linear regression data relative to thallium, rubidium and potassium

x	y	$\bar{x}$	$\bar{y}$	n	r_{xy}	t
Tl	Rb	402	51	53	0·90	15·2
Tl	K	402	2·05	53	0·76	8·3

ppb Tl = 9·946 (ppm Rb) − 103·9
ppm Rb = 0·082 (ppb Tl) + 17·7
per cent K = 0·01 (ppb Tl) + 1·3

n = degrees of freedom; $t'_{1\%}$ for 51 ($n - 2$) degrees of freedom $=2{\cdot}68$.

Table 3. Thallium in various Earth's crust units

	Thallium (ppb)	Rb/Tl	K/ Tl × 1000	
Whole granulite terrain				This work
number of samples	61	53	53	
range	20–2640	80–830	21–362	
average	350	193	145	
Igneous rocks				De Albuquerque and Shaw, 1972
range		19–590	4–112	
average		150	30	
Oceanic tholeiites				De Albuquerque *et al.*, 1972
number of samples	5	5	5	
range	23–63			
average	42	162	96	
Whole Earth's crust				De Albuquerque and Shaw, 1972
average	800			
Upper continental crust				Shaw, 1972
average	800			
Lower continental crust				Shaw, 1972
average	(400)			
Oceanic crust				Shaw, 1972
average	50			

regression analysis data show that the Rb/Tl ratio remains roughly invariant at different Rb levels while the K/Tl ratio decreases strongly with increasing K content. This makes the K/Tl trend similar to the K/Rb trend recognized in the same granulite terrain (Sighinolfi, 1970, 1971) just as in other granulites. In recent years, abundant evidence has accumulated indicating that high-grade granulite facies terrains are depleted in some lithophile elements including K, Rb, U and Th (see a review in Sighinolfi, 1971): from the results of this work conclusions are that thallium also was depleted from granulites at least to the same extent as of rubidium. Mechanisms which have been suggested as the cause of the depletion of elements from deep rocks include anatectic melting, with or without migrating melt phase, and progressive dehydration reactions but the effectiveness of both processes is still far from being known. Thallium data in granulites can contribute to understanding ion transport mechanisms in the deep crust. In igneous processes thallium and rubidium enter the same phases (K-minerals) and Dupuy *et al.* (1973) show that their partition coefficients are about the same in most of the phases. In the course of partial melting, therefore, the two elements may enter the melted fraction in substantially the same proportions and the Rb/Tl ratio would not vary sensibly either in the unmelted residue or in the melt. This would be true whatever may have been the evolutionary course of the partial melting process (i.e. melting and almost complete recrystallization *in situ* or melting followed by migration of the large part of the K-rich melt).

The other mechanism, i.e. dehydration reactions, involves the formation of a fluid phase in which both rubidium and thallium are known to enter and migrate easily, for example, as halides or fluorides (VOSKRESENSKAYA, 1959), but no precise information is yet available on the relative behaviour of thallium and rubidium in a gaseous or aqueous phase in equilibrium with a rock at variable P–T conditions. In the opinion of MAROWSKY and WEDEPOHL (1971), thallium is prevented from major fluid transport by fixation in potassium minerals. VOSKRESENSKAYA and FEL'DMAN (1964) stated that thallium and rubidium become partially separated during alkali metasomatism and thallium is more mobile than rubidium.

On the basis of these considerations, some results of this paper (Rb and Tl depletion rate in respect to K, no apparent fractionation between Rb and Tl in granulite residuals) seem to indicate that partial melting alone could have established the observed Tl–Rb–K trends, even though dehydration reaction effects cannot be excluded completely. Whatever the mechanism of depletion (although more and more evidence suggests that melting plays the major role), according to recent studies by LEWIS and SPOONER (1973), the major depletion of lithophile elements and therefore also of thallium from deep-seated rocks may have occurred in the early stages of crustal evolution rather than by repeated removals through time.

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REFERENCES

DE ALBUQUERQUE C. A. R., MUYSSON J. R. and SHAW D. M. (1972) Thallium in basalts and related rocks. *Chem. Geol.* **10,** 41–58.

DE ALBUQUERQUE C. A. R. and SHAW D. M. (1972) Thallium. In: *Handbook of Geochemistry, II,* (editor K. H. Wedepohl), Chapter 81. Springer, Berlin,

DUPUY C., FRATTA M. and SHAW D. M. (1973) Partition co-efficient of thallium compared with rubidium. *Earth Planet. Sci. Lett.* **19,** 209–212.

FRATTA M. (1973) AAS determination of ppb amounts of Tl in silicate rocks. (Abstr.) 4th Inst. Conf. on Atomic Spectroscopy Soc. Canada, Toronto.

LEWIS J. D. and SPOONER C. M. (1973) K/Rb ratios in Precambrian granulite terranes. *Geochim. Cosmochim. Acta* **37,** 1111–1118.

MAROWSKY G. and WEDEPOHL K. H. (1971) General trends in the behaviour of Cd, Hg, Tl and Bi in some major rock forming processes. *Geochim. Cosmochim. Acta* **35,** 1255–1267.

SHAW D. M. (1972) Development of the early continental crust. Part 1. Use of trace element distribution coefficient models for the Protoarchean crust. *Can. J. Earth Sci.* **9,** 1577–1595.

SIGHINOLFI G. P. (1970) Investigations into the deep levels of the continental crust: petrology and chemistry of the granulite facies terrains of Southern Bahia (Brazil). *Atti. Soc. Tosc. Sci. Nat. Mem.* **A77,** 327–341.

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. (1972) Beryllium in deep-seated crustal rocks. *Geochim. Cosmochim. Acta* **37,** 702–706.

Sighinolfi G. P. (1973) Determination of thallium in geochemical reference samples by flameless atomic absorption spectroscopy. *Atomic Absorption Newsletter* **12,** 136–140.

Sitnin A. A. (1960) Distribution of rare elements in amazonite granites of the Etyka massif, Eastern Transbaikalia. *Geochemistry* (USSR) (English Transl.), **5,** 361–364.

Voskresenskaya N. T. (1959) Geochemistry of thallium and rubidium in igneous rocks. *Geochemistry* (USSR) (English Transl.), **4,** 599–605.

Voskresenskaya N. T. and Fel'dman V. I. (1964) Behaviour of rubidium and thallium during autometasomatism of alkalic granitoids of the Taidut massif (Central Transbaikaliya). *Geochim. Int.* **1,** 56 (abstract).