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GEOCHEMISTRY OF GOLD IN ARCHEAN GRANULITE FACIES TERRAINS

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ABSTRACT

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Gold distribution in Archean—Precambrian granulite facies terrains from Bahia state, Brazil, is investigated by means of flameless A.A. spectroscopy. The average Au content for 105 samples is 1.51 ppb, which is appreciably lower than normal values for intermediate-mafic igneous and sedimentary rocks. Gold distribution is discussed in terms of the possible effects of high-grade metamorphism and the composition of the initial material. Compositional patterns suggest that metamorphism had little influence on primary Au distribution. Alternatively, if Au was mobilized in the fluids generated by dehydration reactions, most of it would have been reprecipitated not far from the starting point. Acid-intermediate igneous and non-mature sediments predominate within the initial material of the Archean granulites.

INTRODUCTION

The purpose of the present paper is essentially two-fold: firstly to present data on Au distribution in high-grade metamorphic terrains, and in this connection to propose some tentative interpretations regarding the behaviour of Au during metamorphism; secondly, to shed new light on the question of the nature of the Archean material which, normally in the form of high-grade metamorphic rocks, is found to constitute the ancient necleii in shield areas. Light may thus be shed on the evolutionary processes of the primitive earth's crust, which are still a matter for conjecture.

Current findings support two main hypotheses regarding the behaviour of Au during regional metamorphism. The first, on account of the frequent association of Au-ore quartz veins with greenschist-facies metamorphic rocks, envisages a certain mobility of Au during metamorphism. Some differences observed in the Au content of rocks of different metamorphic grade (Moiseyenko and Neronskiy, 1968; Moiseyenko et al., 1971) are seen as confirming this view. According to the second hypothesis, Au is inert during regional metamorphism and the content, even in high-grade metamorphic rocks, corresponds to the content in the initial rocks.

This paper presents data on Au distribution in ancient granulite rocks from Bahia state, Brazil.

NOTES ON THE GENERAL GEOLOGY AND PETROLOGY

The samples come from different areas from central-eastern Bahia. Data on the general geology and petrology of some of the areas have already been reported (Fujimori, 1968; Pedreira et al., 1969; Sighinolfi and Fujimori, 1972; Barbosa, 1973). In eastern Bahia the oldest basement formations consist of granulite facies rocks unaffected or only slightly affected by retrograde metamorphism or migmatization that appear as superimposed processes on the same formations towards W Bahia. The granulite terrains extend widely in a N—S direction and have recently been interpreted by Fyfe and Leonardos (1974) as a charnockite belt (Atlantic belt) of a low-pressure type that continues in the African Congo and Angola. Radiometric data (Cordani, 1973) on granulites give ages varying from about 2,600 to 1,000 m.y. with a maximum age frequency at about 2,000 m.y., coinciding with the Trans-Amazonian event. These ages are assumed to date different episodes of granulite facies metamorphism that have occurred in succession, after short periods of retrogradation under amphibolite facies conditions (Fyfe and Leonardos, 1974). Since true-age patterns were obscured by metamorphism, the initial material for granulites may be accepted as being of Archean age.

The great compositional and structural complexity renders any identification of the nature of the pre-metamorphic material very difficult. Indications exist that meta-sediments at least predominate (Fujimori, 1968; Sighinolfi, 1970); nevertheless geochemical studies (Sighinolfi, 1971) revealed some typical magmatic features. Mineralogically, most of the granulites consist of orthopyroxene, clinopyroxene, plagioclase and perthites. Less common are the parageneses with hornblende and/or biotite and with only one pyroxene. Most of the samples considered in this work are typical granulites with charnockite affinities. Details on parageneses different from those reported above are given in Table I.

ANALYTICAL NOTES

Gold was determined by a flameless A.A. procedure previously described by Sighinolfi and Santos (1975). Gold was extracted from HBr solution as bromoaurate with methyl isobutyl ketone (MIBK). This phase was pipetted directly into the graphite tube of the Perkin-Elmer graphite furnace model HGA-2000 coupled with a model 403 spectrophotometer. Analytical sensitivity is about 0.6—0.8 ppb Au for a 1-g sample. Two-gram samples were used for analysis. Experimental error varied between 10 and 50% depending on the absolute Au concentration.

ANALYTICAL RESULTS

Table I reports the results of the analysis of 105 granulite samples indicating also the respective areas of provenance. More than 97% of the samples present Au abundances below 5 ppb, i.e. in the normal range for the majority of igneous and sedimentary rocks. Gold levels are as follows: lower than 0.4 ppb (the determination limit) — 27 samples (25.7%); 0.4—3.5 ppb (normal abundances for igneous rocks) — 72 samples (68.6%); above 3.5 ppb — 6 samples (5.7%). The average Au content is 1.51 ppb if the Au content of the 0.4 ppb samples is taken as 0.2 ppb, dropping to 1.46 ppb if the Au content of these samples is taken as zero. Thus the average Au content for the whole terrain is of the same order as that of acid igneous rocks (see Table II) but is appreciably lower (more than 40%) than averages for most other rock types. This is worthy of note, since published (Sighinolfi, 1970; Sighinolfi and Fujimori, 1972) and unpublished chemical data on granulites from the areas considered show that "intermediate" types predominate over the acid types.

No significant differences in the area distribution of Au are observed; this may be due to the disproportion in the number of samples analyzed from the various areas and to the spread of values observed within a single area. Moreover, no overall relationships between Au abundance and mineral rock composition are apparent, although Au is frequently concentrated in hornblende- and biotite-bearing samples.

GOLD DISTRIBUTION AND HIGH-GRADE METAMORPHISM

The fact that Au levels in the majority of the metamorphic rocks are of the same order as those in common igneous and sedimentary rocks (see Table II) suggests that Au must be relatively inert during regional metamorphism. Nevertheless, as reported in the introduction, results of some studies (Moiseyenko et al., 1971; Petrov et al., 1972) indicate that Au is mobile both during regional and contact metamorphism.

The study of epithermal Au deposits suggests that hydrothermal solutions, not necessarily of igneous origin, appear to have been active in the transport of Au. Both thermodynamic and experimental studies show that Au solubility is appreciable both in alkali chloride and alkaline bisulphide systems. In alkali chloride solutions the solubility of Au as $AuCl_2^-$ or $AuCl_4^-$ increases with HCl molality and temperature (Anderson and Burnham, 1964; Henley, 1972). At high temperatures molecular solutions with gold-chloride complexes are stable (Henley, 1973). Henley (1973) calculates the Au content of hydrothermal solutions derived from metamorphic dehydration reactions in the P—T range of the greenschist-amphibolite facies transition that have leached out all the trace Au in the country rock. The figure found (max. 0.1 ppm Au) indicates that these solutions are strongly unsaturated in relation to the experimentally-determined equilibrium solubilities at temperatures above 350—400°. Thus metamorphism involving dehydration reactions can result in Au redistri-

TABLE I

Gold content in granulite terrains

Sample	Details on mineralogy	Au (ppb)
Itabuna—Ilhéus area (SE Bahia):		
Il 1		<0.4
Il 6	garnet	<0.4
Il 7	biotite—hornblende	0.8
Il 8		2.0
Il 9		0.9
Il 10	biotite—hornblende	2.8
Il 12	biotite—hornblende	1.2
Il 14	anorthosite	0.7
Il 17	anorthosite	<0.4
Il 18		<0.4
Il 19	biotite—hornblende	<0.4
Il 24		<0.4
Il 25		3.1
Il 26		0.8
Il 27		<0.4
Il 28	garnet	1.6
Il 29		1.3
Il 30	biotite—hornblende	0.9
Il 31		1.3
Il 32	biotite—hornblende	4.2
Il 33	biotite—hornblende	1.6
Il 34		0.7
Il 36	biotite—hornblende	0.5
Il 38	amphibolite	<0.4
Il 39	biotite—hornblende	1.8
Il 40	biotite—hornblende	2.0
Il 41	biotite—hornblende	2.0
Il 42		<0.4
Il 43	garnet	1.9
Il 44		0.6
Il 45	biotite—hornblende	0.8
Il 46	biotite—hornblende	2.2
Il 47	biotite—hornblende	2.0
Il 50		0.4
Il 52		<0.4
Il 53		<0.4
Il 54	biotite—hornblende	0.5
Il 55		0.5
Il 56		2.9
Il 57		0.5
Il 58		0.6
Il 59		1.0
Il 60		1.5
Il 61		1.4
Il 62		<0.4
Il 63	garnet	8.1

TABLE I (*continued*)

Sample	Details on mineralogy	Au (ppb)
Il 64	biotite—hornblende	0.8
Il 66		2.3
Il 67		1.4
Il 68		1.4
Il 70		<0.4
Il 71		16.0
Il 72		0.5
Il 73		0.5
Il 76		<0.4
Il 77		2.8
Il 78		16.2
Il 79	amphibolite	<0.4
Il 82	biotite—hornblende	1.4
Il 83		0.8
Ita 1	biotite—hornblende	18.4
Salvador (E Bahia):		
UB 2		<0.4
UB 8	pyroxenite	<0.4
UB 10		<0.4
UB 16		0.6
P 136	biotite	2.3
Itaberaba-Seabra (central Bahia):		
RP 1		1.0
RP 1A		1.0
RP 2		<0.4
RP 3		0.5
RP 3A	hornblende	1.0
RP 3B		0.5
RP 4		0.6
RP 5		0.9
RP 6		2.3
RP 7	biotite—hornblende	<0.4
Itaberaba-Iacù (central Bahia):		
RB 5		0.5
RB 5B		0.5
RB 53		<0.4
RB 78		<0.4
RB 253		1.5
RB 254	biotite—hornblende	4.4
RB 266	biotite	1.7
Senhor do Bonfim (NE Bahia):		
CQ 3		1.1
CQ 5		<0.4
Nanuque (S Bahia):		
ES 13	garnet gneiss	0.8
ES 35	biotite gneiss	0.9
Rio Pardo (S Bahia):		
NP 1		1.0
NP 13		0.8

TABLE I (*continued*)

Sample	Details on mineralogy	Au (ppb)
NP 14		0.4
NP 15		0.5
Rio Salgado (S Bahia):		
NS 4		0.7
NS 5	amphibolite	<0.4
NS 7		1.2
NS 10	biotite gneiss	<0.4
NS 11	biotite—hornblende gneiss	0.4
NS 12		0.5
NS 14		0.7
Various localities:		
JP 48		1.0
GH 17		1.4
P 323		1.1
RP 8		0.8
RP 10		<0.4
P 127	garnet	3.0
P 129		<0.4
Total average (105 samples)		1.51
Standard deviation		2.87
for 27 samples (25.7%)		<0.4
for 72 samples (68.6%)		0.4—3.5
for 6 samples (5.7%)		>3.5

bution, at least within individual beds of rocks, and hence in an increased dispersion, as pointed out by Moiseyenko (1965). Since granulite assemblages are essentially determined by dehydration reactions, the low average Au content found may be due to Au depletion in migratory hydrothermal fluids possibly occurring not only at granulite facies temperatures but also during preceding stages of lower metamorphic grade. Certain factors, for example, abnormally high Au levels in some samples and generalized higher contents in correspondence of hydrated mineralogical parageneses, seem to indicate that Au was redistributed by migration in metamorphic hydrothermal fluids. Unfortunately, since such Au enrichments may be ascribed to primary features of the premetamorphic (igneous or sedimentary) material, the importance of such observations is very limited.

STARTING MATERIAL FOR THE ARCHEAN GRANULITES

Identification of the initial material of Archean granulites is hampered by two factors: firstly, our knowledge of the real constitution and, above all, the growth process of the primitive crust is very limited; secondly, the processes involved in granulite-facies metamorphism (anatexis) normally obscure most

TABLE II

Gold abundances in common rock types (ppb)

	Number of samples	Ranges	Average all analyses	References
Bahia granulites:	105	0.4—18.2	1.51	this work
acid (CaO+MgO 7%)	42		0.57	this work
intermediate (CaO+MgO 7—15%)	51		1.58	this work
mafic (CaO+MgO 15%)	8		0.73	this work
Igneous rocks:				
total acid			0.72	Gottfried et al. (1972)
intermediate and mafic			2.8	Gottfried et al. (1972)
granite	310	0.1—40	1.7	Crocket (1974)
rhyolite	188	0.1—3.5	1.5	Crocket (1974)
intermediate plutonic	261	0.1—110	3.2	Crocket (1974)
mafic plutonic	580	0.3—79	4.8	Crocket (1974)
intermediate-mafic volcanic	696	0.1—48	3.6	Crocket (1974)
oceanic island basalts	4	0.29—1.1	0.50	Crocket et al. (1973)
Sedimentary rocks:				
sandstone and siltstone	105	0.3—12	3.0	Crocket (1974)
shale	28	0.66—8.6	2.5	Crocket (1974)
carbonates	20	0.8—3.9	2.0	Crocket (1974)
deep-sea sediments	28	0.21—17.3	3.4	Crocket (1974)
Metamorphic rocks:				
argillite and slate	135	0.34—10	1.0	Crocket (1974)
schists	114	0.38—9	2.2	Crocket (1974)
gneisses	37	0.2—22	3.9	Crocket (1974)

of the primary features. This does not occur, as is well known, under lower metamorphic grade conditions.

In any case, structural and compositional features suggest that the Archean material that formed the granulite terrains in Bahia state consisted of a mixture of igneous and sedimentary rocks in unknown proportions. Since average Au levels are significantly different in the main igneous rock types (see Table II), Au distribution may be of a certain importance in investigating the starting material for Archean granulites, providing this distribution has not been unduly affected by metamorphism. Because of their complex nature, granulites cannot be classified chemically as in the case of igneous rocks. The total silica sometimes used as parameter to discriminate different granulite rock types (Lambert and Heier, 1968; Sighinolfi, 1970) is largely unsatisfactory, because: (1) acid igneous and detritical (quartz-rich) sediments appear within a single group; and (2) silica may be mobile during metamorphism. In view of the average composition of most igneous and sedimentary rocks (Wedepohl, 1969, pp. 227—271), the sum CaO+MgO was chosen to classify granulites chemically, taking into account their possible starting material. In fact, both Ca and Mg are accepted as being inert elements during metamorphism, and the sum CaO+MgO increases regularly from acid to mafic igneous and affords satisfactory discrimination of the main sedimentary rock types. Thus granulites are divided (rather arbitrarily) into three groups with CaO+MgO < 7, 7—15 and > 15%, respectively. The first group comprises most of the acid igneous rocks (Nockolds, 1954), sandstones and mature sediments (pelagic clays and geosyncline shales), the second intermediate igneous and platform shales and the third mafic igneous rocks. Graywackes figure mainly in the second group. Of the samples of granulites analyzed, the "intermediate" predominates over the "acid" type, while mafics are negligible. Gold distribution in the different groups of granulites is represented in Fig.1. In calculating the average Au contents in the various groups the > 5-ppb samples were excluded so as not to unduly falsify the real figures. The results obtained (see also Table II) show that the average Au content increases markedly (from 0.57 to 1.58 ppb) from acid to intermediate granulites and seems to decrease in mafic granulites (0.73 ppb), although the latter value is hardly indicative on account of the low number of samples analyzed. The findings of many authors (Gottfried et al., 1972; Tilling et al., 1973; Crocket, 1974) would suggest that Au distribution in granulites as a whole may be regarded as a typical magmatic trend. This would at first sight seem to imply that acid-intermediate igneous rocks predominate in the initial material of Archean granulites, in accordance with the "tonalite" model recently proposed by Windley (1975).

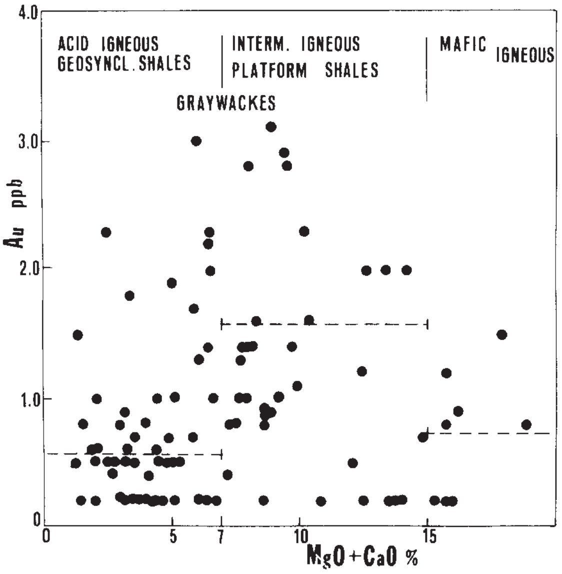

Fig.1. Variations of gold in granulites as a function of the CaO + MgO content (> 3.5-ppb Au samples not represented). Dashed lines: partial averages.

The effect that the possible sedimentary component may have had on Au distribution is hard to evaluate, for Au contents vary widely within a given sedimentary rock type, and occur in frequently contrasting patterns. Crocket (1974), for example, affirms that conglomerates and sandstones normally tend to be richer in Au than other sediments, especially carbonate rock and pelagic sediments. On the other hand, Pchelintseva and Fel'dman (1973) found an elevated Au content in para-amphibolites formed by metamorphism from clay-carbonate beds, while silica-rich meta-sediments had the lowest content. In our case, most of the higher Au contents in acid-intermediate granulites are quasi-systematically correlated with high MgO/CaO ratios and sometimes with elevated TiO_2 contents. The MgO/CaO ratio in most of the acid-intermediate igneous rocks is quite uniform and generally lower than 0.5 (Wedepohl, 1969). Of the sediments, graywackes and geosyncline shales present much higher MgO/CaO ratios (greater than unity). Few Au determinations have been carried out in graywackes, but the data available (Boyle, 1961) reveal high Au contents probably related to the mafic detrital components. Since granulites with a high MgO/CaO ratio are not infrequent among the samples analyzed, it can be deduced that a sedimentary component of a graywacke type may be present, and even abundant, within the starting material of the Archean granulites. This accounts for the observed Au distribution patterns on the one hand, and, on the other, agrees with models for the growth of the primitive crust (Engel et al., 1974) according to which sedimentation patterns underwent considerable change (from non-mature to mature types) from Archean to Proterozoic in concomitance with major chemical changes (e.g. of the Na/K ratio) in the main rock types.

Finally, with reference to the relatively low average content of Au throughout the granulite terrains, it should be pointed out that since the igneous trend of Au is undoubtedly a pre-metamorphic feature, metamorphism does not seem to have affected Au abundances. The initial Archean material for granulites would therefore appear to contain less Au than present-day material. An alternative explanation is that Au was partially mobilized by metamorphism without the primitive patterns being destroyed. This is feasible only in the case that Au solubility in the fluids deriving from dehydration reactions is extremely limited (in disagreement with the experimental results discussed above) or if most of the Au present in the leaching fluids was re-deposited in loco or after migration over short distances.

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