TRACE ELEMENTS CHARACTERIZATION OF THE HYDROTHERMALLY DEPOSITED TANZANITE AND GREEN GROSSULAR IN THE MERELANI -LELATEMA SHEAR ZONE, NORTHEASTERN TANZANIA

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Received 20 June 2000: Accepted: 26 November 2002

ABSTRACT

Geochemical investigations of trace element contents of different rock samples were determined in the late Proterozoic metamorphic sequences of the Mozambique Belt along the Merelani–Lelatema shear zone, northeastern Tanzania. The area is composed of the following rock types: pelitic and semi-pelitic gneisses, psammitic, hydrothermally altered including carbonate-rich, carbonate-gypsum-rich, and iron-rich rocks, pegmatite dykes and crystalline limestones. Trace element characteristics of the principal rock units in and outside the shear zone have been compiled and studied. With the exception of higher barium contents in pelites, trace element contents in the psammitic and pelitic gneisses show some similarities while in the hydrothermally altered rocks where gemstones (tanzanite and green grossular) are localized reveal that the following trace elements: Ba, Cu, Mo, Ni, Rb, Sr, U, V and Zn have been enriched, while As, Ag, Co, Cr, Cs, Pb, Th and Zr were relatively depleted compared to the other rock types. Calculated Cl/ Br ratios are at maximum of 900, which are the same as found in waters of deep drill holes and in salt waters associated with oil deposits. Calculated Co/Ni ratios are low, less than unity in most rocks except the psammitic gneisses and carbonate-rich rocks whose values are approximately 3.4 and 6.5 respectively. The low Co and Ni values in these rocks may be a result of low $a_{co}2+$ *and* $a_{ni}2+$ *in the hydrothermal fluids and / or lower temperature of crystallization. The high V contents result in an unusual degree of V substitution in a number of silicate and oxide phases. The high levels of V in the metasediments, together with that of Ni and Sr, is reflected in their enhanced concentration in the hydrothermally altered zone indicating that they may have been partly re-distributed by the hydrothermal fluids. Vanadium contents in the hydrothermally altered rocks are strongly enriched especially in the calcium-magnesium-aluminium-rich rocks but low in carbonate-sulphate-rich rocks. It is most likely that at the stage when tanzanite and green grossular were crystallized Al, Ca, Mg, Si, and V were migrating together and were incorporated into the minerals precipitated. Vanadium* (V^{3+}) *substitutes for iron* (Fe^{3+}) *and aluminium* (Al^{3+}) *diadochically in the crystal lattices of silicates mainly zoisite and green grossular.*

The data suggest that the gemstone deposits are the result of a sequence of long-continued and overlapping geological processes culminating in intense shearing, considerable mobilization of trace elements and syn-tectonic hydrothermal intrusion.The Proterozoic metasedimentary rocks of the shear zone, as well as those enclosing it, served as the source of trace elements, while diffusion *of the trace element constituents and their precipitation in physico-chemically favorable traps, formed in response to folding and shearing, resulted in the gemstone deposition.*

INTRODUCTION

The geochemical processes, which control the natural behaviour of trace elements in minerals, are not properly known but many researchers have used trace elements as genetic indicators for some mineral deposits (Hawley & Nichol 1959, Loftus-Hills & Solomon 1967). Migration of water and other volatiles from wet country rocks into relatively dry magmas has been suggested on theoretical grounds by Kennedy (1995), Khadik and Khitarov (1965) and Szadeczky-Kardoss (1966). Shieh and Taylor (1969) have shown similar migration of trace element bearing water of country and intrusive rocks based on oxygen isotope composition. Other workers who have suggested that exchange of various major and minor constituents between magmas and country rocks include Goldschmidt (1958), Evans (1964), Brookins and Dennen (1964), Ghose (1966, 1970) and Oba (1968). This paper evaluates the importance of element exchange, by determining the distribution of Ag, As, Ba, Co, Cu, Cr, Li, Mo, Mn, Ni, Pb, Rb, Sr, Th, U, V, Zn, Zr, Cl, and Br, in the hydrothermal zone and in country rocks of the Merelani-Lelatema shear zone. The mechanism of element transport in country rocks and hydrothermal solution is discussed, and an attempt is made to show that element exchange between them may have an important bearing on the formation of gemstone deposits genetically related to hydrothermal solution intrusions.

General Geology

The structural map of the volcanic province along the Rift System in NE Tanzania showing the Lelatema fault and collected sample locations are shown in Fig.1.. Accordingly, the shear zone is a long zone of overthrust along the northeast-southwest bending along the northwest-southeast trending limbs of the major folded limb of the Proterozoic geoanticle and the thrusting marks the culmination of a series of fold movements directed from NNE to SSW. Some kilometers of steeply folded rocks consisting of pelitic and semi-pelitic, psammitic gneisses, dolostones, hydrothermally altered rocks, quartzo-feldspathic rocks, pegmatite dykes, and soils are present in the zone. Regional metamorphism resulted in the crystallization of quartz, albite, muscovite, chlorite and carbonates, and was followed by the intrusion of hydrothermal solutions along the Lelatema fault and its fissure zones. Contacts of hydrothermally altered rocks with the metasedimentary rocks along the fault zone are sharp and chilled. Evidence at this zone shows that large masses of country rocks were engulfed by the hydrothermal solutions and thus silicification, kaolinitization, sericitization, albitization and chloritization are processes that have occurred. The hydrothermally altered zone resulted in various mineral assemblages of muscovite, plagioclase, potassium feldspar, quartz, zoisite, grossular and addition of iron oxyhydroxides. In some places, development of pegmatite dykes, quartz veins and intense silication occurred.

Retrograde metamorphism later affected rocks of about half the contacts and resulted in rehydration, addition of K_2O and alteration of biotite, and feldspars to colorless micas, chlorite, albite, leucoxene, and other fine-grained clay minerals.

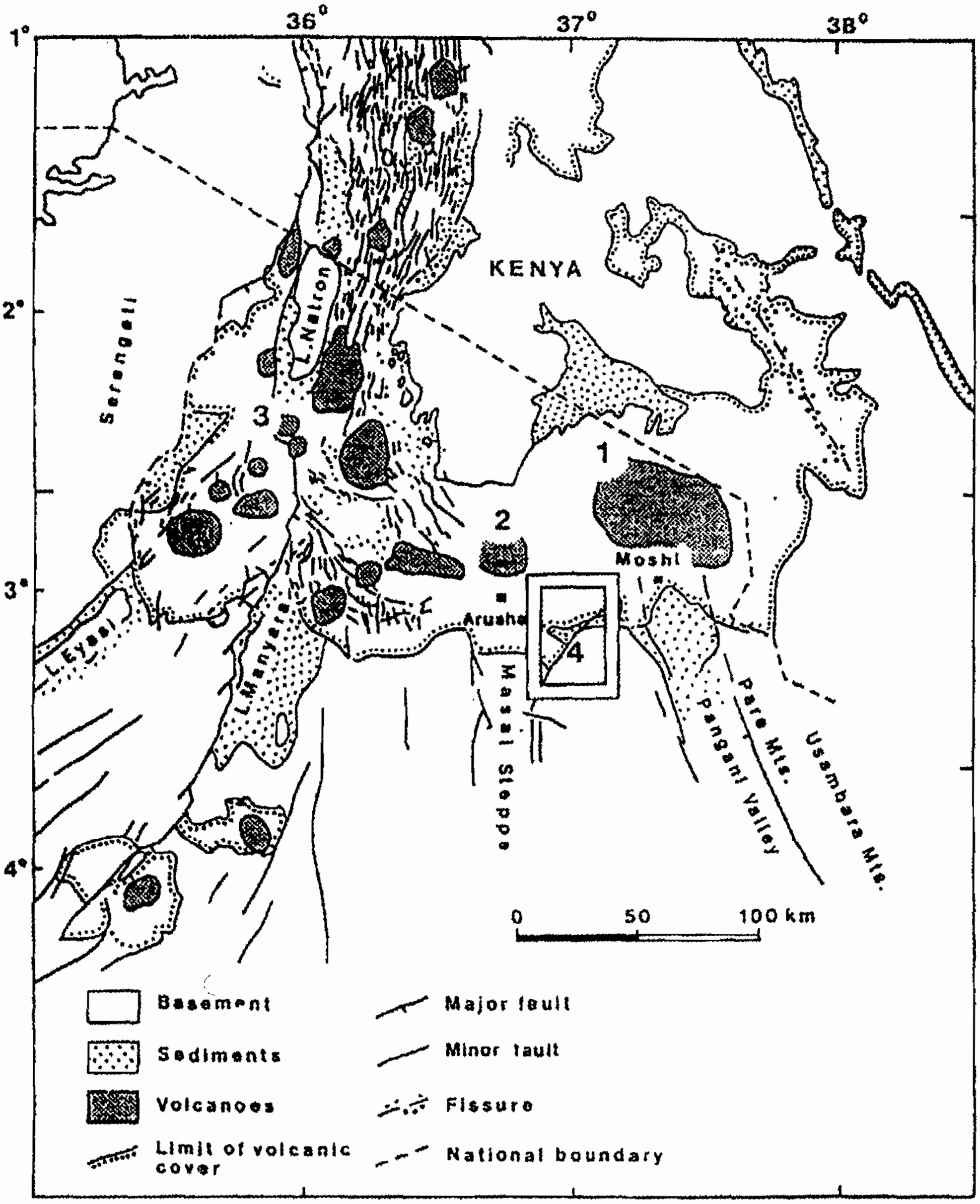

Fig.1. The structural map of the volcanic province along the Rift System in NE Tanzania showing the extent of the Cenozoic cover (sediments and volcanogenic material), the principle volcanic centers, and the distribution of large faults (Fairhead 1980; cf. also Rosendahl 1987. 1) Mt. Kilimanjaro, 2) Mt. Meru, and 3) Mt. Lengai. The square (4) represents the Merelani- Lelatema area.

Shear Zone Rocks

The rocks lying within and adjacent to the shear zone consist of a thick pile of northwesterly dipping pelitic gneisses with interbanded psammitic rocks. In the central sector the zone is mainly represented by medium to fine-grained thin bands of hydrothermally altered rocks (Malisa 1987). These are graphite-rich and due to variation in mineralogical composition and coloration by the altered minerals, the rocks are divided into: hydrothermally altered carbonate-rich, carbonate-gypsum-rich, iron-rich, calc-silicates, pegmatites and quartz veins (Fig.2). The rocks show varying coloration and amounts of opaque minerals, biotite and muscovite and accessory minerals being chlorite, epidote rutile and zircon. Tanzanite and green grossular are found within the calc-silicate rocks in boudins or fold hinges associated with quartz veins.

Structures

The rocks show imprints of structural elements of different generations (Malisa and Muhongo 1990). A complete structural reconstruction is, however, possible through a systematic traverse across the belt. The shear zone is characterized by a dominance of transposition schistosity and strain-slie cleavage that have developed through continuous deformation of earlier axial plane schistosity. Microstructural studies on micas and chlorite, which have also formed along the shear planes, clearly support this tectonic sequence (Malisa & Muhongo 1990). The most important linear structure is a down-slip NNE to ENE trending lineation (striation and mineral elongation) that determines the direction of slip and unrestricted tectonic transport, with quartz microfabric around this lineation. When the shear movements came into halt, the end of tectonic activities in this belt was marked by post-shear cross-faults displaying not only the rocks of the shear zone but also those adjacent to it.

Shearing caused extensive mylonitization and the various processes of feldspathization, hydrothermal reconstitution and mineralization is found to have distinct time-place relationship with the shear tectonics of the belt (Malisa & Koljonen 1987). Feldspathization took place mainly during the closing phase of shear movements whereas the rocks in the zone have undergone hydrothermal alteration, with host-rocks chloritization largely syn-tectonic to shearing. Like-wise, gemstone mineralization is also sympathetically guided by the structural characteristics of the shear zone, because there is a statistically significant regional tendency of most mined tanzanite to be in pockets in boudins or folded hinges along these shear zones (Malisa & Koljonen 1986). These structural traps formed in response to shearing and it may well be suggested that the optimum structural deformation within the shear zone essentially determine the ideal environment for the gemstone localization (Malisa *et al.* 1986).

Sampling and Spectrochemical Analysis

Over one hundred samples were collected from the Merelani – Lelatema area. These include pelitic and semi-pelitic, psammitic gneisses, marbles, quartzites, pegmatite dykes, hydrothermally altered rocks, calc-silicates and soils. Trace element analyses were determined by inductively coupled argon plasma spectrometry (ICAP) and neutron activation analysis method in the chemical laboratories of GSF in Espoo, Finland using Jarrell-Ash Plasma Atom MK II spectrometer (Noras & Wansen 1985) and Reactor Laboratory of the Technical Research Center of Finland by the method described by O'Neil and Suhr (1960), Rosenberg and Zilliacus (1977). Au and Pd were determined using Perkin Elmer 2280 with HGA-50 graphite oven at the GSF Rovaniemi Laboratory (Kontas 1981, and Kontas *el al.* 1987).

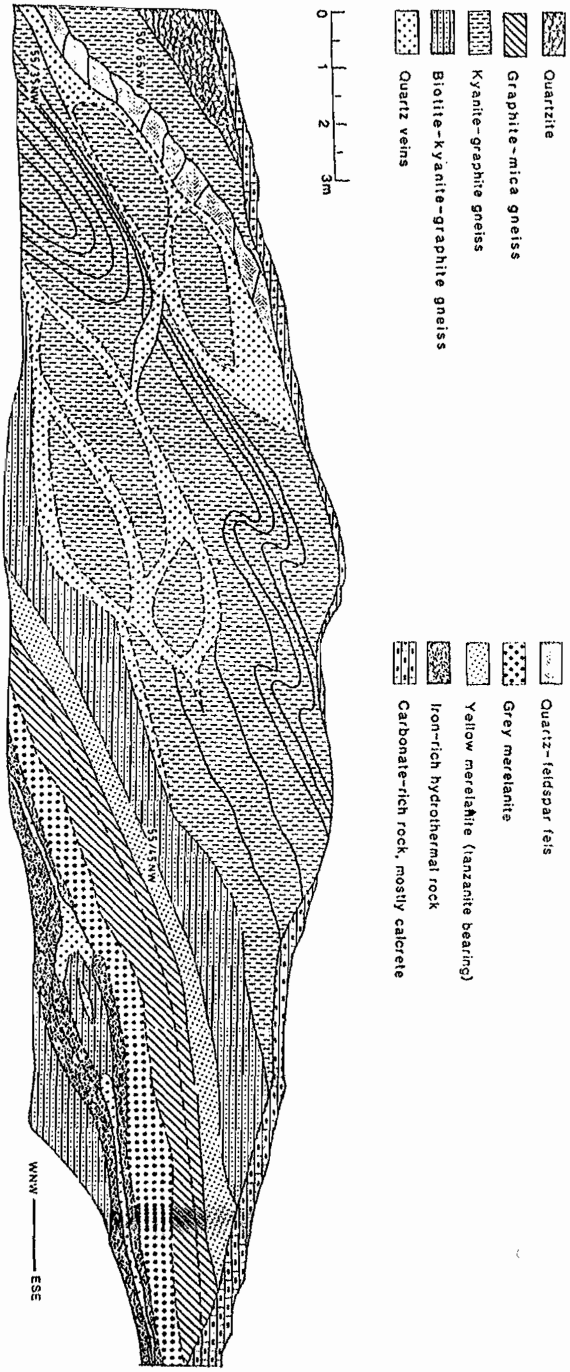

Fig.2. Detailed geological map of the Merelani area showing the different lithological units.

RESULTS

Analytical results are given in Tables 1-7. Calculated element ratios are presented in Table 8. The average values have been compared with averages reported on the Earth's crust and similar rocks in literature (Rosler & Lange 1972, Ahrens 1977). The highest values of each element were investigated separately in the different lithological units and deductions made. Comparison of trace element in corresponding parts of different rocks and the hydrothermally altered zone, using distance from the hydrothermal intrusion outer edges as unity, and other distances calculated as multiple or fraction of this, and detailed statistical analysis are however, discussed in another publication (Malisa in prep.1). Further, some details on the possible geological processes, which may have affected the rocks in the area, are useful in the interpretation and thus the reader is referred to another publication (Malisa 1987).

Trace element Geochemistry

Trace element determinations of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, U, V, Zn, and Zr were made on 80 representative samples. The range of variation and the average concentrations of the fourteen trace elements are presented in Tables 1-7. The trace element abundance and their distribution patterns in the shear zone are discussed in the following manner:

Arsenic. The concentration of arsenic is very low. Since arsenic occurs in nature in oxidation states –3, 0, +3 and +5, it forms a variety of compounds e.g. Arsenides, sulphides, oxides, arsenates, arsenites and sometimes in native states (Koljonen 1992). During the migration with hydrothermal solutions, arsenic was slightly depleted in the shear zone within the contact between iron-rich rocks and psammitic gneisses (Table 2 & 5). This element has no direct relationship to the gemstone deposition as no trace arsenic has been observed in the gemstone analysis (Malisa *et al.* 1986). However, the contents are the same or lower than the mean for the Earth's crust. During the migration with hydrothermal solutions, arsenic was probably somewhat enriched into the iron-rich hydrothermal rocks (2.3 ppm).

Barium is normally considered to be captured by potassium bearing phases (Rankama & Sahama 1950). Barium could be admitted by calcium particularly in feldspars formed at high temperature (Heier 1973). Accordingly, the Ca/Ba ratio in a differentiated sequence should decrease with fractionation at low temperatures. However, the maximum concentration of this element is exceptionally high 5130 ppm in pegmatites 5160 ppm in pelitic and semi-pelitic gneisses and 2810 ppm in psammitic gneisses and low 73 ppm in gypsum bearing rocks. Due to the sulphate ion, it was incorporated to form $BaSO_4$ and thus could not migrate in the hydrothermally altered zone, thus it is found in high concentrations.

Caesium contents are low, but are somewhat enriched into micas within the pegmatities (13 ppm). A similar process has probably occurred along the Mozambique belt, where economic caesium-rich pegmatites containing pollucite are exploited (Knorring 1970; Malisa in prep.2).

Cobalt. The range of concentrations of this element is low; 40 ppm, 220 ppm, 33 ppm, 7 ppm, 5.9 ppm, 12.8 ppm and 13 ppm in the pelitic and semi-pelitic gneisses, psammitic gneisses, pegmatites, hydrothermally altered rocks, iron-rich rocks, carbonate-gypsum rich rocks and carbonate-rich rocks respectively c.f. Tables 1-7. Cobalt is depleted in the rocks and minerals in the hydrothermal zone and their Co/Ni ratios are also low c.f. Table 8. Compared to Ni, there is no correlation. This may be due to the fact that Ni^{2+}, unlike Co^{2+}, is in a different spin state than Fe^{2+} in the iron-bearing minerals and possibly has a different covalent radius.

Co/Ni ratios of around 17.1 have been used to support a volcanic exhalative origin of mineralization (Bajwah et al. 1987).

Copper. The range of concentrations of this element is wide, and its average value is 44 ppm in the hydrothermally altered rocks and 60 ppm in iron-rich hydrothermally altered rocks. Through experimental studies, Krauskopf 1956 has shown that $Fe(OH)_3$ and clay minerals effectively absorb copper. The source of copper may be traced to the oxide–bearing sediments rich in Fe. Copper in the oxidizing environment is controlled much more by the adsorption of iron oxyhydroxides in clay minerals and inorganic matter rather than by simple precipitation. Copper is enriched mainly in the iron-rich rocks.

Table 1: Trace element contents in pelitic and semi-pelitic gneisses

Element	Number of Samples	Range (ppm)	Mean (ppm)	St. Deviation
Ag	15	4-5	4	± 1.25
As	10	0-9.6	1.9	± 1.50
Ba	10	90-5160	2430	± 1560
Co	15	11-130	40	± 58
Cr	15	50-470	165	± 110
Cs	15	0.4-10	2.6	± 4.2
Cu	10	10-130	42	± 39
Mo	10	2-56	40	± 22
Ni	15	17-520	130	± 155
Pb	9	3.3-14	10.1	± 6.0
Rb	7	17-92	50	± 28
Sr	18	60-850	210	± 170
Th	10	1-20	12	± 8
U	12	2-130	37	± 37
V	18	160-3600	850	± 840
Zn	10	10-450	200	± 345
Zr	13	120-340	271	± 105
Cl	10	1-12.5	10	± 6.6

Table 2: Trace element contents in psammitic gneisses

Element	Number of samples	Range (ppm)	Mean (ppm)	St. Deviation
Ag	5	1.1-7.6	6	± 1.8
As	8	0.3-4.7	205	± 1.7
Ba	10	20-3470	1770	± 1180
Co	14	34-344	220	± 96.0
Cr	16	56-490	160	± 105
Cs	10	0.7-10	6.9	± 5.4
Cu	13	10-250	50	± 75
Mo	7	40-60	50	± 10
Ni	15	7-260	64	± 67
Pb	10	17-120	44	± 41
Rb	8	17-20	19	± 2
Sr	17	70-520	185	± 120
Th	9	10-11	10	± 1
U	10	10-50	27	± 16
V	13	40-1260	510	± 390
Zn	12	10-430	70	± 110
Zr	13	10-340	210	± 100
Cl	6	0.3-14.5	10	± 7.2
Br	7	0.5-1.5	1	± 0.1

Table 3: Trace element contents in pegmatites

Element	Number of samples	Range (ppm)	Mean (ppm)	St. Deviation
Ag	8	0.4-6.7	5	± 0.02
As	8	0.6-1.3	0.9	± 0.3
Ba	8	620-5130	2600	± 1730
Co	8	15-42	33	± 13.2
Cr	8	10-170	90	± 50
Cs	8	12-14	13	± 8.8
Cu	8	10-50	20	± 17
Mo	8	1.5-36	24	± 10.6
Ni	8	20-80	36	± 24
Rb	8	18-203	180	± 106
Sr	8	180-800	460	± 260
Th	8	0.1-9.6	8	± 6.9
U	8	10-40	19	± 12
V	8	70-520	310	± 136
Zn	8	10-200	60	± 75
Zr	8	50-580	180	± 190
Cl	8	0.3-1.9	1.7	± 0.8
Br	8	0.5- 2.5	1.6	± 0.2

Table 4. Trace element contents in hydrothermally altered rocks

Element	Number samples	Range	Mean	St. Deviation
Ag	10	0.6-6.6	4	± 0.5
As	10	0.6-1.9	1.3	± 0.7
Ba	10	30-3600	1660	± 1600
Co	10	0.5-8.7	7	± 4.6
Cr	10	60-170	90	± 40
Cs	10	0.2-0.5	0.4	± 0.2
Cu	10	10-120	44	± 46
Mo	10	30-64	47	± 24
Ni	10	90-1060	430	± 350
Pb	10	10-20	15	± 7
Rb	10	10-83	50	± 36
Sr	10	170-380	250	± 90
Th	10	10-12	11	± 11.3
U	10	10-50	24	± 16
V	10	600-1420	990	± 290
Zn	10	70-840	410	± 300
Zr	10	150-320	230	± 70
Cl	10	0.7-206	180	± 1055.0
Br	10	0.1-1.9	1.0	± 0.35

Table 5: Trace element contents in iron-rich rocks

Element	Number of samples	Range (ppm)	Mean (ppm)	St. Deviation
Ag	7	0-3	0.4	± 1.21
As	7	1.4-3.4	2.3	± 1.0
Ba	7	30-770	203	± 260
Co	7	0-40	5.9	± 2.46
Cr	7	43-180	80	± 19.2
Cs	7	8-12	10	± 48
Cu	7	40-120	60	± 36
Mo	7	6.6-110	60	± 73
Ni	7	210-4020	1560	± 1540
Pb	7	0-10	4.0	± 2.3
Rb	7	0.3-40	4.7	± 2.2
Sr	7	30-360	190	± 130
Th	7	1.6-10	2.6	± 2.6
U	7	3-120	40	± 48
V	7	290-7040	3300	± 2710
Zn	7	10-4780	1900	± 1560
Zr	7	10-300	170	± 100
Cl	7	5-280	180	± 31.2
Br	7	0-0.3	0.2	± 0.33

Table 6: Trace element contents in carbonate-gypsum-rich rocks

Element	Number of samples	Range (ppm)	Mean (ppm)	St. Deviation
Ag	5	3-4	3.3	± 2.1
As	5	0.1-5.3	1.7	± 1.0
Ba	5	18-30	23	± 5.0
Co	5	4-19	12.8	± 29
Cr	5	1-62	19	± 25
Cs	5	0.1-0.2	0.15	± 2.3
Cu	5	10-60	18.6	± 17.1
Mo	5	0.7-5.5	10	± 19
Ni	5	30-70	42	± 29
Pb	5	0-20	4	± 12.5
Rb	5	4.4-20	7.9	± 14.1
Sr	5	30-96	52	± 32.2
Th	5	2-10	7.7	± 37
U	5	6-21	15.9	± 12
V	5	10-96	44	± 16
Zn	5	25-60	36	± 4.6
Zr	5	1.2-10	6	± 55.2
Cl	5	0-410	188	± 102
Br	5	0.2-1.1	0.68	± 0.3

Table 7. Trace element contents in carbonate-rich rocks

Element	Number of samples	Range (ppm)	Mean (ppm)	St. Deviation
Ag	10	0.1-4	1.2	± 0.9
As	10	0.1-5.3	1.7	± 1.7
Ba	10	20-1640	240	± 440
Co	10	4-22	13	± 7
Cr	10	1-1950	180	± 490
Cs	10	<0.3-0.8	0.5	± 0.2
Cu	10	10-60	20	± 16.0
Mo	10	7-32	18	± 9.0
Ni	10	160-1950	790	± 630
Pb	10	0.20	2.0	± 1.7
Rb	10	4.4-9.4	6	± 1.55
Sr	10	70-1060	270	± 250
Th	10	0.8-8.0	3.8	± 3
U	10	6-40	16	± 11
V	10	12-1100	380	± 360
Zn	10	10-2780	940	± 830
Zr	10	7.6-430	110	± 120
Cl	10	0-410	41	± 32.6
Br	10	0.2-1.1	0.6	± 0.4

Table 8: Calculated element ratios in different rocks from Merelani tanzanit mining area

Rock type	Cl/Br	Co/Ni	Ni/Co
Pelitic & semi pelitic gneisses	5.6	0.3	3.3
Psammitic gneisses	10	3.4	0.3
Pegmatites dykes	1.1	0.9	1.1
Hydrothermally altered	180	0.02	61.4
Iron-rich rocks	900	0.002	264.4
Carbonate-gypsum rich rocks	276.5	0.31	3.3
Carbonate-rich rocks	58.3	6.5	60.7

Chromium. The range of concentrations of chromium is wide, and its average value is 90 ppm along the hydrothermally altered zone, but it is slightly enriched in carbonate-rich rocks. Chromium almost exclusively occupies octahedral sites in the silicate phase into which it substitutes (Burns & Burns 1975). The sedimentary enrichment of Cr is readily explained because Cr^{3+} closely resembles Al^{3+} and Fe^{3+} in ionic radius and the chemical behavior. During weathering Cr^{3+} is thus concentrated into the clay minerals by substituting for Fe^{3+} or Al^{3+} (Thayer 1973). While the concentration of Cr within sediments through the clay fraction is common, Cr may also be added directly in pyroxenes (Van de Kamp & Leake 1985). However, chromium is depleted in the hydrothermally altered zone.

Lead. The average concentration of lead is very low in the hydrothermal zone (15ppm). Unlike copper, it seems that lead has not migrated in hydrothermal solutions because of the presence of carbonate and sulphate ions. It has no significant relation with strontium, vanadium or copper (Tables 4-7).

Molybdenum. The concentration of molybdenum is slightly elevated 40 and 50 ppm in pelitic and psammitic gneisses respectively, 24 ppm pegmatite dykes, 47ppm along the hydrothermally altered rocks and 60 ppm in iron-rich rocks c.f. Tables 1-5. As with vanadium, it is suggested that the origin of the two elements is due to the enrichment with organic matter during sedimentation.

Nickel. The average concentration of Ni is high (430 ppm) and concentration range is very wide. In rocks (Ni^{2+}) forms silicates and sulphides and replaces magnesium and iron in mineral lattices. In magmatic processes it tends to behave like magnesium and iron and is removed from silicate melt at an early stage when olivine, pyroxenes, and amphiboles crystallize into ultramafic and mafic rocks (Koljonen 1992). During magmatic differentiation the Ni/Co ratios decreases, being 1 in granites, 18 in ultramafic rocks and 3 in gabbros (Turekian & Wedepohl 1961). However, the Ni/Co ratios in the studied area are low except in the hydrothermally altered rocks especially the iron-rich rocks c.f. Table 8. A positive relation exists between Ni and Zn. The ferromagnesian phases are the chief hosts of this element. Transient rise in the concentration of this element in the iron-rich rocks is caused by pronounced crystallization of the mafic phases and impression of plagioclase precipitation.

Rubidium. In general the concentration level of rubidium should fall along with removal of calcium and correspondingly barium should rise with fractionation (concomitant with absolute increase of potassium in residual liquid). It is possible that K/Rb ratio also K/Cs ratio maybe affected by preferential escape of fugitive elements being activated by volatiles. Rubidium in the studied area is the same or lower than in the Earth's crust and in slates. Like caesium, rubidium is enriched into micas in pegmatites. Rubidium seems to have a slight increase in the hydrothermally altered rocks.

Silver contents are very low (4-6 ppm) in all the rocks analyzed. Comparatively, there is an increase of this element in the hydrothermally altered rocks. Silver seems to migrate poorly in carbonate-bearing solutions and is not incorporated in the iron-bearing rocks.

Strontium. The concentration range of strontium is relatively wide and the average value is 250 ppm in hydrothermally altered rocks. Its relation to cobalt and lead is negative. In the studied area, strontium is mostly enriched in micas within the pegmatites (460-ppm) and (270-ppm) in carbonate-rich rocks. Strontium is enriched in the calc-silicate rocks along the hydrothermal zone. Hurlbut (1969) reports 0.05 wt.% SrO in tanzanite. Strontium, which has a higher radius than calcium, is admitted to calcic phases and the Ca/Sr ratios should fall with differentiation (according to Goldschmidt's rule) if admittance to potassic phases is not significant. With the appearance of alkali feldspar, strontium is captured by the phase, besides being admitted to calcic minerals. Geochemical behaviour of strontium is in many respects intermediate between that of barium and calcium. However, the entry of strontium in the crystallites is controlled by the relative dominance of different factors e.g. temperature of the melt, availability of the element, structural states of the precipitating solids, relative activity of capture and admittance in the silicates. Accordingly, Ca/Sr ratios at certain stages maybe erratic.

Thorium contents are low and in the hydrothermally altered zone the same as the average in slates (Rosler & Lange 1972). Relatively, low values of thorium are observed in the hydrothermally altered rocks.

Uranium. The values of uranium concentrations found in the studied area are higher than found in sediments and main types of igneous rocks (Turekian & Wedepohl 1961). The average concentration of uranium in psammo-pelitic rocks is 32ppm, in pegmatites, 19ppm, in hydrothermal and carbonate-rich rocks, 20ppm, and in iron-rich rocks, 40 ppm. Uranium occurs as uraninite in contacts of pegmatites and hydrothermally altered rocks and is more enriched in the iron-rich hydrothermally altered rocks. The uranium results show that there is essentially no difference between the metasedimentary rocks (Table 1 and 2). The mean values in the data suggest that the highest concentrations of uranium are found in iron-rich hydrothermally altered rocks near pegmatities. Most of the uranium is present in the resistate fraction and to some extent it is occurring in the oxyhydroxide fraction.

Vanadium. The range of concentration of vanadium is very wide and its average value is exceptionally high (3300 ppm) in iron-rich and (990 ppm) in the hydrothermally altered rocks. The contents are higher than usually found in similar rocks and sediments (Turekian & Wedepohl 1961). Since the country rocks are rich in graphite, vanadium migrated during metamorphism and was incorporated into the crystal lattices of silicates (Landner 1986). Like uranium and molybdenum, it has been enriched into the sediments with the organic matter during sedimentation (Malisa 1998). However, along the hydrothermal zone the contents of vanadium were increased in the iron-calcium-magnesium-aluminium-rich rocks (Tables 4 –7). During the crystallization of zoisite and grossular, Ca, Mg, Si, Al, and V were migrating together and were incorporated into these minerals (Malisa *et al.* 1986). This indicates that vanadium is relatively enriched in ferric iron which maybe a reflection of increasing water content of the residual liquid in the hydrothermally altered rocks. Malisa *et al.* (1986) reports 0.26 and 0.10 wt.% V_2O_3 in tanzanite and grossular respectively. However, V_2O_3 in zoisite is 0.01 wt.%.

Zinc. The average concentration of zinc, being 410ppm, in the hydrothermally altered zone is much higher than lead (15 ppm). The range of concentration of this element is very wide c.f. Tables 1-7. The source of this element may be oxide-bearing sediments and has migrated to the hydrothermal zone in processes similar to processes that produce hydrothermal zinc deposits from sediments and sedimentary rocks (Barnes 1979). Zinc is known to be enriched in hydrothermal solutions (Muffler & White 1969).

Zirconium. The average concentration of zirconium being 240 ppm in the psammo-pelitic gneisses and 190 ppm along the hydrothermally altered rock is slightly higher than found in the Earth's crust. Higher enrichment is found in sediments.

DISCUSSIONS

The rocks in the studied area have been affected by a sequence of long-continued and overlapping geological processes such as faulting, intense shearing, folding, considerable mobilization of trace elements and syn-tectonic hydrothermal intrusion. As a result most of the rocks in the area are strongly weathered.

An attempt has been made to compare and contrast the average concentration of certain trace elements in different lithological units and the hydrothermally altered zone. The distribution of trace elements shows that later processes may have elevated the concentration gradients produced in the hydrothermal zone by trace element exchange with the country rocks. Psammo-pelitic gneisses, which envelop the hydrothermal zone, are in both sides bounded by crystalline limestone. The gneisses are graphite-rich and are relatively enriched in Ba, Sr, V and Zr but relatively poor in As, Ag, Co, Cr, Cs, and Th (Tables 1 and 2). Characteristic to the area is that the hydrothermal zone seems to have been enriched in the following elements: Ba, Cu, Mo, Ni, Rb, Sr, U, V and Zn while As, Ag, Co, Cr, Cs, Pb, Th and Zr, are depleted (Table 1-7). Comparatively, Ba, Cr, Ni, Sr, V, Zn, Zr, migrate easily with carbonate-rich solutions while V, Ni, Zn, As, Cu, Mo, were incorporated in the iron oxyhydroxides and enriched in iron-rich rocks (Table 5 & 7). It is suggested that these elements migrate poorly in carbonate–sulphate-rich solutions (Table 6). Within the hydrothermally altered rocks where pegmatites and iron-rich rocks occur, the elements Ba, Ni, Sr, V, Zn, and Zr are enriched. Possible interpretation for the observed distribution of these elements includes migration from the other lithological units towards the hydrothermally altered zone. The concentration of vanadium, nickel and zinc has increased in the hydrothermally altered zone especially in the iron-rich rocks possibly partly as a result of silica loss. The concentration of arsenic in psammitic gneisses (205 ppm) is much higher than in argillaceous schists and this indicate that the metasediments in the area originate from clay-rich sediments.

CONCLUSIONS

The hydrothermally deposited gemstones at the Merelani-Lelatema area are unusual on account of the high vanadium, strontium and nickel contents in both the gemstones and their host rocks, together with the widespread development of spectacularly coloured blue and green vanadium-bearing silicates in the sheared zone. Strontium and nickel were enhanced, above levels normally encountered in sediments, by sedimentary processes except in the gypsum-rich rocks. They were probably incorporated in the sediments both in the clay-mineral component and sand derived from the detrital Proterozoic terrain. The high background vanadium levels throughout the metasediments, resulted, during metamorphism, in the stabilization of unusually high degree of vanadium substitution in a number of common metamorphic silicate phases.

Results presented in this paper suggest that under hydrothermal conditions, in carbonate-rich fluids, vanadium appears to be mobile, as evidenced by the presence of vanadium-bearing tanzanite and green grossular in quartz veins and vugs. Due to tectonic movements, the hydrothermally altered rocks are enriched in some trace elements especially vanadium, strontium and nickel by intergranular diffusion from the country rocks into the hydrothermal zone and, to a lesser extent, by assimilation. Diffusion took place in the direction of decreasing activity, both within the contact of hydrothermal zones, and the country rocks. The mobility of these elements is probably influenced by their activity and the sign of enthalpy change of the reaction governing their volatilization, which indicates their direction of diffusion. The concentration of fluids rich in elements associated with epigenetic deposits is generally greater in metasedimentary rocks (especially shales) than hydrothermally altered rocks and this is why gemstone deposits are associated with the tectonically and hydrothermally intruded metasedimentary rocks. Finally, the colorful gemstone-bearing veins and vugs are a result of post-metamorphic diffusion processes between adjacent graphite-rich psammo-pelitic gneisses and crystalline dolostone layers, with the silicate phases, growing as a result of the diffusive fluxes, absorbing the sedimentary vanadium already present in the rocks. However, these deposits reflect the existence of unique geological processes in the area, probably processes that are different from those encountered in other high-grade metamorphic terrains.

ACKNOWLEDGEMENT

The author wishes to thank the University of Dar es Salaam, Faculty of Science and the Geological Survey of Finland for the support of this work. The financial support by SIDA/SAREC to carry out the research work is thankfully acknowledged.

REFERENCES

Ahrens LH 1977 Origin and distribution of the elements. Pergamon Press. 909pp

Bajwah ZU, Seccombe PK and Offler R 1987 Trace element distribution, Co:Niratios and genesis of the Big Cardia iron-copper deposit, New South Wales, Australia. *Mineral Deposita* **22**: 292-300

Barnes HL 1979 Solubilities of ore minerals. In Barnes HL (Ed.) Geochemistry of hydrothermal ore deposits, 2nd edition 400-460. New York: John Wiley

Burns VM & Burns RG 1975 Mineralogy of chromium. *Geochim. Cosmochim. Acta,* **39**: 903-910

Brookins DG and Dennen W H 1964 Trace element variation across some igneous contacts. *Trans. Kansa* ***Acad. Sci.*** **67**: 70-91

Evans BW 1964 Fractionation of elements in the pelitic hornfelses of the Cashel-Lough Wheelaun intrusion, Connemara, Eire. *Geochim. Cosmochim. Acta* **28**: 127 – 156

Fairhead JD 1980 The structure of the crosscutting volcanic chain of northern Tanzania and its relation to the East African Rift System. *Tectonophysics* **65**: 193-208

Ghose NC 1966 Behaviour of trace elements during thermal metamorphism and or granitization of the metasediments and basic igneous rocks. *Geol. Rundschau* **55**: 608-617

Ghose NC 1970 Geochemistry of thermal metamorphism and granitization processes in aureole rocks around Richughuta Dt. Palamua, Bihar, India. *Geol. Rundschau* **59**: 686-724

Goldschmidt V M 1958 Geochemistry. London Oxford University Press. 730 p

Hawley JE and Nichol I 1959 Selenium in some Canadian sulfides. *Econ. Geol.* **54**: 608-628

Heier KS 1973 Geochemistry of granulite facies rocks and problems of their origin. *Phil. Trans. Roy. Soc., London* **A, 273**: 429-442

Hurlbut CS Jr 1969 Gem zoisite from Tanzania. *Am. Min.* **54**: 702-709

Khadik A A and Khitarov N I 1965 Effect of pressure on the exchange of water between magma and the enclosing rocks. *Geochem. Int.* **2**: 397-406

Kennedy GC 1995 Some aspects of the role of water in rock melts. Spec. pap. *Geol. Soc. Am.* **62**: 489-503

Knorring O von 1970 Mineralogical and geochemical aspects of pegmatites from orogenic belts of equatorial and southern Africa, pp.157-184. In African magmatism and Tectonics, (TN Clifford and IG Gass, eds.), Oliver & Boyd, Edinburgh, 461 p

Koljonen T 1992 Geochemical atlas of Finland, Part2: Till. Geological Survey of Finland. 218p

Kontas E 1981 Rapid determination of gold by flameless atomic absroption spectrometry in the ppb and ppm ranges without organic solvent extraction. *At. Spectosc.* **2**: 59-61

Kontas E Niskavaara H and Virtasaalo J 1987 Flameless atomic absorption determination of gold and palladium in geological references samples. *Geostand Newsl.* **10**: 10-15

Krauskopf KB 1956 Separation of manganese from iron in the formation of manganese deposits in volcanic association. *XX Int. Geol. Cong. Manganese Symp.* **1**: 119-131

Landner L 1986 Speciation of metals in water, sediments and soil systems. Edited by Somdev Bhattacharji, Gerald M. Friedman, Host J. Neugebauer and Adolf Seilacher. Springer-Verlag-Berlin-Heidelberg

Loftus-Hills G and Solomon M 1967 Cobalt, nickel, and selenium in sulphides as indicator of ore genesis. *Mineral. Deposita* **2**: 228-242

Malisa E, Kinnunen K and Koljonen T 1986 Notes on fluid inclusions in vanadiferous zoisite (tanzanite) of the Merelani area, Northern Tanzania *Bull. Geol. Soc. Finland* **58**: 53-58

Malisa E and Koljonen T 1986 Paragenesis of tanzanite (zoisite) in the Merelani area, NE Tanzania. Poster presentation. Abstracts, 7th Int. assoc. on the ore genesis of ore deposits. Symp., Nordkalott Project Meeting 18-22nd August, Lulea, Sweden

Malisa E, Kinnunen K and Koljonen T 1986 Notes on fluid inclusions in vanadiferous zoisite (tanzanite) of the Merelani area, Tanzania. *Bull. Geol. Soc. Finland* **58**: 53-58.

Malisa E and Koljonen T 1987 Structural control of the tanzanite deposits of the Merelani area in the Lelatema Mountains, northeastern Tanzania. Oral presentation. Abstracts, IGCP Project 247. Int. Conf. on "Precambrian Metallogeny Related to Tectonics and Computerized Mineral Resources Assessment. Methods Applied to Metallogenic Provinces. Dec. 7-19th Arusha, Tanzania, pp.35-36

Malisa E 1987 Geology of the Tanzanite Gemstone Deposits in the Lelatema area, NE Tanzania. Ph.D. Thesis 160 p.

Annales Academiae Scientiarum Fennicae 111, Geological-Geographica.

Malisa E and Muhongo S 1990 Tectonic setting of gemstone mineralization in the Preterozoic metamorphic terrain of the Mozambique Belt in Tanzania. *Precambrian Research* **46**: 167-176

Malisa E 1998 Application of graphite as a geothermometer in hydrothermally altered metamorphic rocks of the Merelani-Lelatema area, Mozambique Belt, Northeastern Tanzania. *Journal of African Earth Sciences,* **26(2)**: 313-316

Malisa E (in prep.1) The statistical and systematic use of trace element analysis of geochemical data of the Merelani tanzanite mining area, North Eastern Tanzania

Malisa E (in prep2) Mineralogy of the Merelani area, North Eastern Tanzania

Muffler LJP and White DE 1969 Active metamorphism of Upper Cenozoic sediments in the Salton Sea geothermal field and the Salton Trough, Southern-eastern California. *Geol. Soc. Am., Bull.* **80**: 157-182

Noras P and Wansen G 1985 The application of ICAP spectrometry in geochemical mapping. 10th Nordic Atomic Spectroscopy and Trace element Conference, August 6-9, 1985, Turku

Oba N 1968 Interchange of chemical components between granitic intrusion and Aureole rocks of South Kyushu, *Japan. J. Geol.* **76**: 371-381

O'Neil RL and Suhr NH 1960 Determination of trace elements in lignite ashes. *Appl. Spectrosc.* **14**: 45-50

Rankama K and Sahama T G 1950 Geochemistry. University of Chicago Press. 912 pp

Rosenberg R J and Zilliacus R 1977 Improving accuracy in routine instrumental activation analysis. *J. Radioanal. Chem.* **39**: 189-200

Rosendahl BR 1987 Architecture of continental rifts with special reference to East Africa. *Ann. Rev. Earth. Planett. Sci.* **15**: 4455-503

Rosler HJ and Lange H 1972 Geochemical tables. Elsevier Publishing Company. Amsterdam-London-New York. p. 238

Shieh Y N and Taylor Jr H P 1969 Oxygen and hydrogen isotope studies of contact metamorphism in the Santa Rosa Range, Nevada and other areas, *Contr. Mineral. Petrol.* **20**: 306-356

Szadeczky-Kardoss E 1966 On the migration of volatiles and chemical changes at igneous contacts. *Acta Geol. Hung.* **10**: 263-283

Thayer TP 1973 Chromium. In: Brobst, D.A. & Pratt, W.P. (ed.) United States Mineral Resources. *U.S. Geol. Surv. Prof. Papers* **820**: 111

Turekian KK & Wedepohl KH 1961 Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am., Bull* **72**: 175-192

Van de Kamp PC & Leake BE (1985) Petrography and geochemistry of feldspathic and mafic sediments of the northeastern Pacific margin. *Trans. R. Soc. Edinburgh Earth Sci.* **76**: 411-449