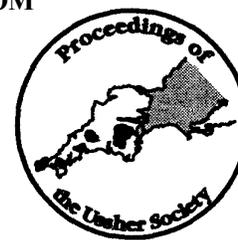


COLUMBITE-TANTALITE, RUTILE AND OTHER ACCESSORY MINERALS FROM THE ST AUSTELL TOPAZ GRANITE, CORNWALL

P.W. SCOTT, R.D. PASCOE AND F.W. HART

Scott, P.W., Pascoe, R.D. and Hart, F.W. 1998. Columbite-tantalite, rutile and other accessory minerals from the St Austell topaz granite, Cornwall. *Geoscience in south-west England*, **9**, 165-170.



The topaz granite in the area west of Nanpean is geochemically different from and younger than the biotite granite, lithium mica granite and tourmaline granite, which make up the major part of the St Austell granitoid pluton. Kaolinization has released the accessory minerals from the host granite, and these fine grained minerals (up to 100 μm) separate into the hydrocyclone underflow waste during the production of china clay. The accessory minerals can be concentrated further by gravity separation. Topaz, columbite-tantalite, Nb-Ta rutile, cassiterite and apatite are the major phases. Zircon, monazite, Fe oxide, Mn-ilmenite, pyrite, arsenopyrite and sphalerite also occur, but wolframite is absent and uranium-bearing phases are only found very rarely as inclusions in other minerals. The columbite-tantalite shows considerable variation in Nb/Ta and Fe/Mn ratios, and the rutile varies in its Nb, Ta and Fe contents. The data may be interpreted as arising from simultaneous crystallisation of the two minerals on a pseudo-binary solid solvus. Two types of Ce-rich monazite are found. Th-poor monazite and the absence of uranium minerals may be accounted for by mobilization of Th and U during kaolinization. Cassiterite is considered to have a magmatic origin in the topaz granite. The Fe oxides and sulphides most probably come from from cross-course mineralization in the china clay pits. As with other similar evolved granites elsewhere in the world, the topaz granite and the waste tailings dams in the St Austell area, in which the accessory minerals from past extraction of kaolinized granite now reside, should be considered potential sources for Nb, Ta and Sn metals.

P.W. Scott and R.D. Pascoe, Camborne School of Mines, University of Exeter, Redruth, Cornwall TR15 3SE

F.W. Hart, Goonvean Ltd, St Stephen, St Austell, Cornwall PL26 7QF

INTRODUCTION

The extraction of china clay from the St Austell Granite involves washing the pit face with water from a high pressure hose. This causes disaggregation of the kaolinized granite, releasing the minerals into a stream of water. A combination of spiral or bucket wheel classifiers, hydrocyclones and settling tanks are used to separate the kaolin clay products from the other minerals which go to waste tips or fine tailings lagoons (cf. Bristow and Exley, 1994). The mineralogy of the waste is dominated by quartz, micas, tourmaline and unaltered feldspars. It also contains the accessory minerals from the granite. Generally these are of small grain size (up to 100 μm), have a high specific gravity, and they separate preferentially into the hydrocyclone underflow waste product during processing. This product is an ideal source of material for the study of the accessory mineral assemblage in the kaolinized granite.

The present study was made on the waste from two china clay pits, Goonvean and Rostowrack. Both are within the topaz granite (Figure 1). The accessory mineral assemblage separated from the waste is described. It is rich in columbite-tantalite, rutile and cassiterite with minor amounts of apatite, zircon and monazite. There is a wide range of chemical variation shown by the columbite-tantalite and rutile, and two types of monazite occur. The high amounts of Nb, Ta and Sn make it worthwhile considering these metals as potential by-products from china clay extraction.

GEOLOGICAL BACKGROUND

The St Austell Granite has a number of magmatic units of which the topaz granite (Manning and Hill, 1990; Bristow and Exley, 1994; Manning *et al.*, 1996), previously called the equigranular Li-mica granite (Type E) incorporating fluorite granite (Type F) (Exley and Stone, 1982) and non-megacrystic Li-mica granite (Manning and Exley, 1984), is probably the youngest. It occurs to the west of Nanpean (Figure 1), and both Goonvean and Rostowrack china clay pits are wholly within this granite. A small body is also present at Hensbarrow. The topaz granite has been described by Manning and

Hill (1990) and Manning *et al.* (1996). It contains quartz, lithium mica and two feldspars, albite and K-feldspar. X-ray data by the present authors show the latter to be microcline. A euhedral-subhedral fluorine-rich topaz is characteristic (Manning and Hill, 1990). Fluorite and tourmaline also occur, although the latter is insignificant compared to that found within some of the other granite types. The range of accessory minerals in the topaz granite given by Manning *et al.* (1996) are apatite (Mn-bearing), amblygonite, zircon, Nb-Ta-Ti oxides (columbite/ ilmenorutile) and uraninite. Different assemblages of accessory minerals are found in the biotite granite, lithium-mica granite and tourmaline granites, which make up the remainder of the St Austell pluton (Manning *et al.*, 1996). Nb/Ta minerals are not reported from these granites, accessory minerals being monazite, zircon, apatite and rutile, along with uraninite in the biotite granite. Three microprobe analysis of ilmenorutile, one of which is from the Nanpean topaz granite, are given by Manning and Hill (1990). These show variable amounts of Ti, Fe, Nb and Ta, along with minor Si, Sn and W.

Geochemically the topaz granite is enriched in Li and Rb, relative to the surrounding granites, and it has a much higher Nb/ Zr ratio (Hill and Manning, 1987; Manning *et al.*, 1996). This and other data led Manning and Hill (1990) and Manning *et al.* (1996) to conclude that the topaz granite is not comagmatic with the other granites in the St Austell pluton, but is a consequence of a second stage of crustal melting.

The topaz granite is variably kaolinised in Goonvean and Rostowrack china clay pits. Some unkaolinised granite exists, notably in parts of the pits or in adjacent areas which are and were used for china stone extraction. Apart from pervasive kaolinisation, alteration of the granites in these pits has involved minor greisenising, some vein and stockwork tourmaline/fluorite mineralisation, veining by kaolinite and pale green smectite, and Fe-rich cross course and later felsite dyke (elvan) emplacement. Unlike several other china clay pits within the Li-mica granite, there is only very minor evidence of Sn mineralisation in these pits.

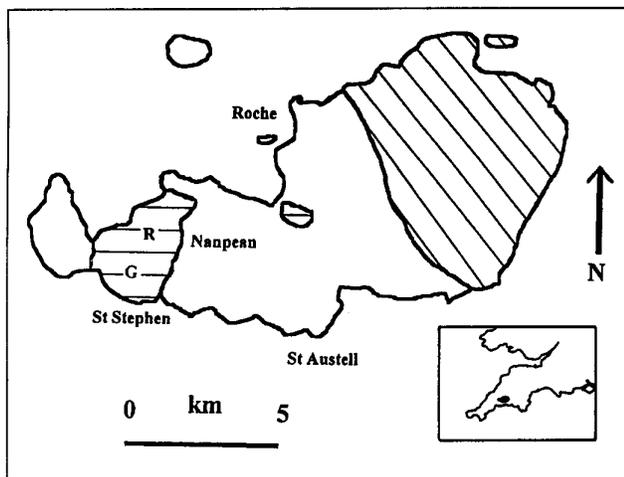


Figure 1. Geological map of the St Austell Granite, showing location of Goonvean (G) and Rostowrack (R) china clay pits. Geology simplified after Bristow and Exley (1994). Diagonal ornament: biotite granite. Horizontal ornament: topaz granite with pockets of fluorite granite. No ornament: Li granite with some biotite granite. Inset map of south-west England shows the position of the St Austell Granite.

SAMPLES AND ANALYTICAL TECHNIQUES

Four samples of waste were taken from the hydrocyclone underflow, three from the processing plant at Rostowrack pit and one from that at Goonvean pit. As extraction of the china clay involves the washing of one or more areas of the pit at any one time, and there is a time delay before the water rich slurry reaches the hydrocyclone, the samples cannot be located precisely. They are taken to represent typical material from kaolinised topaz granite. The samples were de-slimed, and the dense accessory minerals separated using two stages of gravity concentration. In the first stage a laboratory shaking table was used to process a 3kg sample generating a rough concentrate (50-100 g). This was then further upgraded using a Mozley table to produce a 'clean' product.

The chemistry of some elements within the accessory mineral concentrates was determined by X-ray fluorescence spectrometry (XRF) (Philips PW1400) using a fusion bead techniques. Some trace elements of 26 samples of topaz granite from Rostowrack pit, the adjacent Great Wheal Prosper china stone quarry, and the disused Tregargus quarry, also in the topaz granite, were also determined by XRF, using pressed powder pellets. The major mineral phases in the accessory mineral concentrates were identified initially by X-ray diffraction (Siemens D5000) using $\text{CuK}\alpha$ radiation. Scanning electron microscopy (JEOL 840 and Oxford Instruments Link AN 10000 energy dispersive spectrometer) was the main technique used in describing and identifying individual grains and crystals and in spot mode the same instrument was used for quantitative microanalysis using a ZAF4 correction procedure. Detection limits for elements in the quantitative microanalyses are: (all in % by weight) TiO_2 , 0.20; FeO , 0.33; MnO , 0.21; CaO , 0.17; P_2O_5 , 0.65; Nb_2O_5 , 0.37; Ta_2O_5 , 0.26;

Sample	R1	R6	R11	G6
%				
Nb_2O_5	10.5	11.8	11.6	5.9
Ta_2O_5	3.4	3.7	3.3	1.9
TiO_2	9.6	15.3	21.4	5.4
SnO_2	3.3	1.5	5.1	2.8

R1, R6 and R11 from Rostowrack pit. G6 from Goonvean pit.

Table 1. Chemistry of accessory mineral concentrates

Sc_2O_3 , 0.22; La_2O_3 , 0.48; Ce_2O_3 , 0.45; Pr_2O_3 , 0.50; Nd_2O_3 , 0.49; Sm_2O_3 , 0.41; ThO_2 , 0.57; UO_2 , 1.39; Y_2O_3 , 0.63. These limits are higher than is achievable with an electron microprobe using energy dispersive analysis, and as the design and geometry of a scanning electron microscope is not optimised for fully quantitative microanalysis, the accuracy and precision is lower. A combination of real and virtual (for Sc, Nb, Pr, Nd, Sm, Th and U) standards were used for calibration. Accuracy and precision were ensured and non-conforming analyses discarded by monitoring the X-ray beam stability; by repeating analysis of the Co reference standard regularly; checking data against the accepted chemical formula for the mineral; checking for zero residual X-ray counts after data processing; and obtaining an acceptable total for the analysis, appropriate allowance being made for O and other low atomic number elements which may be present, but cannot be determined. Thus, the data are considered of sufficient quality to report quantitative analyses and to show variations in the mineral chemistry.

CHEMISTRY

The amounts of Nb, Ta, Ti and Sri oxides in the accessory mineral concentrates separated from the hydrocyclone underflow are given in Table 1. Significant quantities of each of these elements are present. Si and Al from topaz make up the bulk of the remainder. There are some differences between samples from Rostowrack pit and also between Rostowrack and Goonvean pits. However, the element ratios are relatively consistent throughout, the differences being largely dilution effects from other elements. This suggests that there is some homogeneity in the distribution of Nb, Ta, Ti and Sn within the kaolinised granite. This relationship would probably not exist if, for example, Sn were preferentially concentrated in mineralised veins, and not disseminated throughout the granite body.

Data for Nb, Ta, Ti and Sn and some other trace elements in the unkaolinised topaz granites are given in Table 2. Some additional data for the topaz granite in the Nanpean body are taken from Manning and Hill (1990). Where elements were determined both for this study and in Manning and Hill (1990), the data are closely similar, except that Manning and Hill (1990) report slightly more Nb (51-63 ppm), and less Y (6-21 ppm) and Zr (17-25 ppm). They also show more but consistent amounts of Sn in the granite (21-25 ppm). These differences are more likely to be due to inter-laboratory incompatibility, than to differences between samples. Thus, the data indicate there is little variation in the trace elements between different samples, confirming a homogeneous topaz granite source area for the heavy accessory minerals.

MINERALOGY

The accessory mineral concentrates are made up almost entirely of grains of single minerals. Aggregates are rare. Four main minerals of different reflectivities are recognisable in polished grain mounts under the reflected light microscope. In increasing reflectivity these are silicate phases of low reflectivity (mainly topaz), cassiterite, columbite-tantalite and rutile. The size of grains ranges from 10-300 μm , varying a little between samples, but the bulk of the grains in each sample is 40-100 μm . Cassiterite grains are commonly smaller than grains of the other phases. Topaz and cassiterite are identifiable in X-ray powder diffraction patterns, but columbite-tantalite and rutile are recognisable as ferrocolumbite (ICDD card 33-0659) and ilmenorutile (ICDD card 31-0646) respectively. There is some line broadening in the X-ray diffraction peaks from these two minerals as would be expected from minor differences in the unit cell sizes arising from variable chemistries.

Estimates of mineral proportions are given in Table 3, based on counting grains (approx.150) in polished mounts using the scanning electron microscope. Varying amounts of topaz, columbite/tantalite and ruffe are dominant, with apatite common in two samples. The proportion of cassiterite is broadly comparable with the chemical

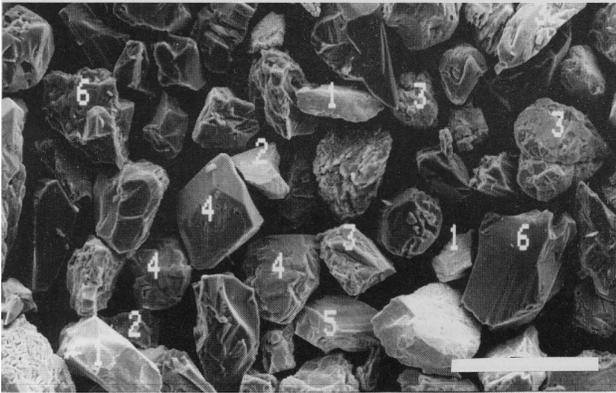


Figure 2. Scanning electron micrograph of grains from the heavy mineral concentrate. Scale bar = 100 μm . Numbered grains as follows: 1, columbite-tantalite; 2, cassiterite; 3, rutile; 4, apatite; 5, zircon; 6, topaz.

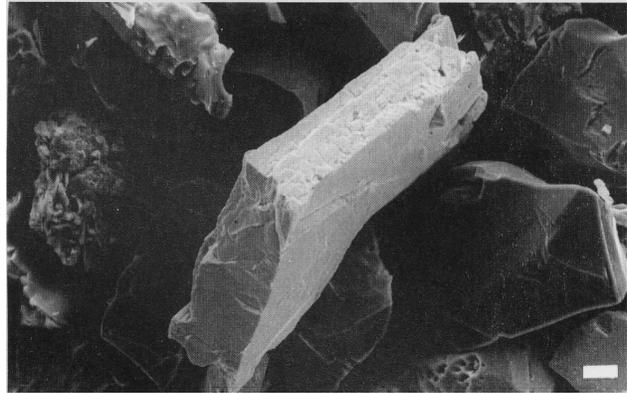


Figure 3. Scanning electron micrograph of prismatic columbite-tantalite crystal. Scale bar = 10 μm .

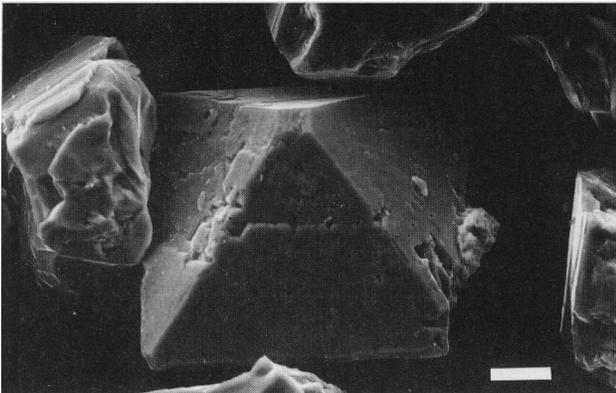


Figure 4. Scanning electron micrograph of rutile crystal showing pyramidal and basal pinacoid termination. Scale bar = 10 μm .

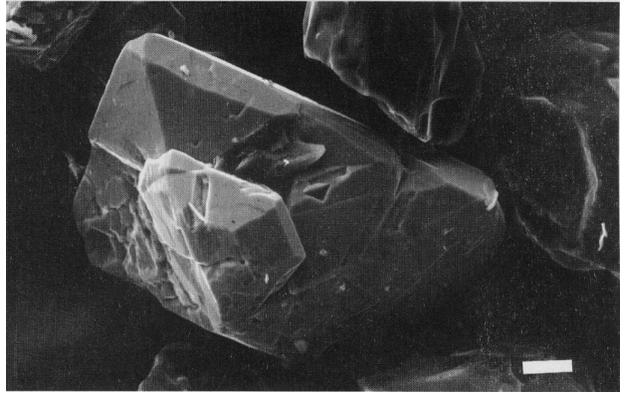


Figure 5. Scanning electron micrograph of cassiterite crystal showing prism and pyramid faces. Prominent notch on upper right edge may indicate a twin plane. Scale bar = 10 μm .

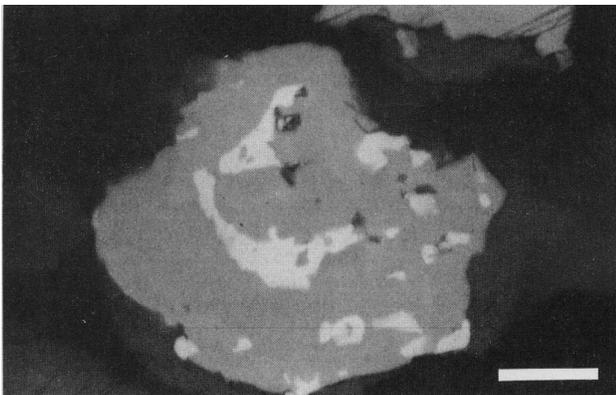


Figure 6. Scanning electron micrograph in back-scattered mode of polished grain of rutile with inclusions of columbite-tantalite. Scale bar = 10 μm .

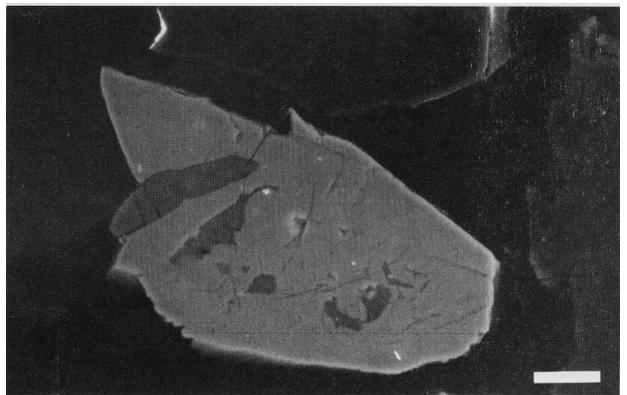


Figure 7. Scanning electron micrograph in back scattered mode of polished grain of columbite-tantalite with inclusions of rutile. Scale bar = 10 μm .

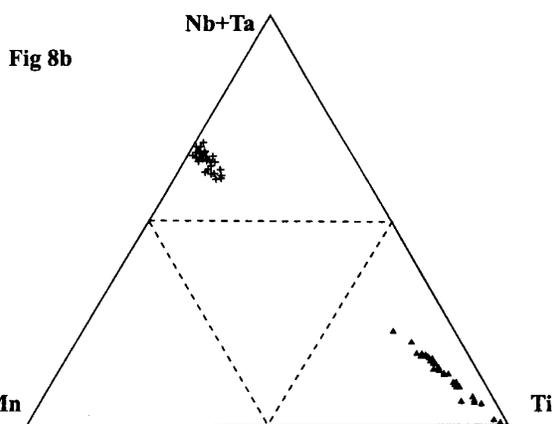
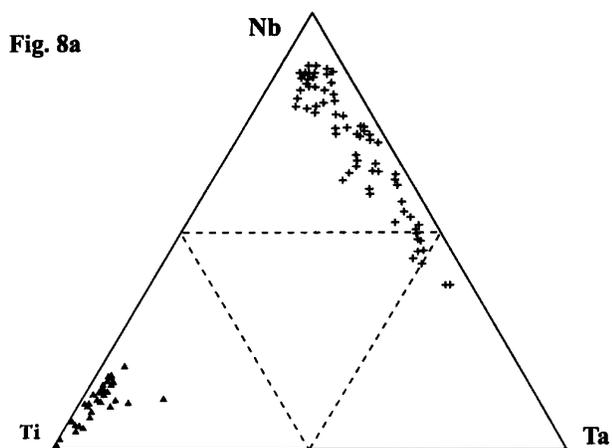


Figure 8. a. Triangular plot of atomic ratios of Nb, Ta and Ti for columbite-tantalite (+) and rutile (▲) analyses, b. Triangular plot of Fe+Mn, Nb+Ta and Ti for columbite-tantalite (+) and rutile (▲) analyses.

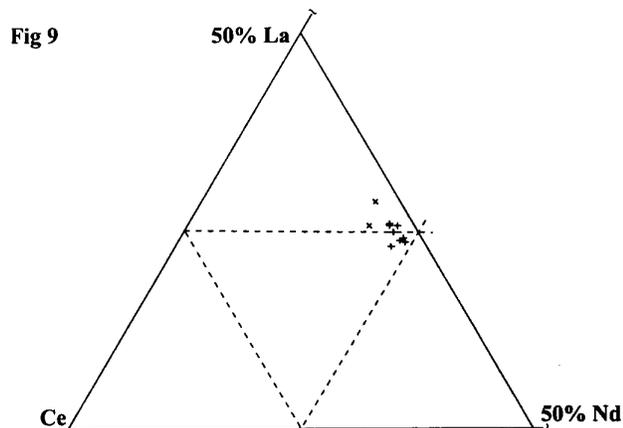


Figure 9. Triangular plot of atomic ratios of La, Ce and Nd for monazite analyses. +, Th-bearing monazite. ., Tb-free monazite.

values for SnO₂. More accurate correlation could only be expected if many more grains were counted and size and density segregation of minerals during preparation of the polished blocks were avoided. Zircon is the only other mineral present in amounts greater than 1%. Additionally, monazite, fluorite, tourmaline, Fe oxide, Mn-ilmenite,

		mean	s.d.	n	range
TiO ₂	%	0.03	0.02	26	nd - 0.06
Nb	ppm	38	5	26	27-50
*Ta		30	14	12	nd - 59
Sn		nd		26	
*W		17	13	6	5-41
Th		6	3	26	nd - 10
*U		14	3	6	9-17
Y		110	35	26	47-180
Zr		39	4	26	36-44
La		7	3	26	nd - 13
Ce		15	1	26	13-19
Nd		13	3	26	9-18

sd: standard deviation. n: number of analyses. *: Data from Manning and Hill (1990). nd below detection limit (5ppm for trace elements, 0.01% for TiO₂).

Table 2. Trace element data for the topaz granite.

pyrite, arsenopyrite and sphalerite can be found. Rarely pyrochlore and uraninite occur as inclusions in columbite grains. Wolframite, which is common in cassiterite bearing veins in some china clay pits, was not found. As amblygonite, which has a specific gravity (SG) of 3.0-3.1 (Klein and Hurlbut, 1993), is absent from the concentrates, and tourmaline (SG 3.0-3.25) and fluorite (SG 3.18) are only present in minor amounts, the separation process appears to have been an effective method for the concentration of minerals with specific gravities greater than 3.2.

Scanning electron micrographs of some grains are shown in Figures 2 to 5. The grains occur either as angular fragments or as crystals showing well developed faces. Some almost perfect crystals of topaz and rutile are found, both showing prism and bi-pyramidal faces. Columbite-tantalite is typically lath-shaped with well developed prism faces, and in some cases appears corroded. Occasionally cassiterite, apatite and zircon occur with well developed faces. Intergrowths of columbite-tantalite and rutile are visible in polished sections of the grains, both of columbite-tantalite surrounding rutile and vice-versa (Figures 6 and 7).

MINERAL CHEMISTRY

The columbite-tantalite ((Fe,Mn)(Nb,Ta)₂O₆) shows considerable differences in chemistry between grains, representative analyses being given in Table 4. Within grains, zoning is mostly insignificant. Nb is usually in excess over Ta, but there is a continuous variation from Nb_{0.80-1.80} and Ta_{0.09-1.17} atoms per formula unit. About one in ten grains has Ta>Nb, necessitating such grains being named tantalite rather than columbite. Fe and Mn also show a continuous variation between Fe_{0.19-0.81} and Mn_{0.07-0.73} atoms per formula unit. However, the Ta/Nb and Fe/Mn substitutions appear to be independent of each other. Minor amounts of Ti (0.05-0.20 atoms) and Sc (up to 0.05 atoms) are also present.

Representative analyses of rutile and ilmenite are given in Table 4. There are variable amounts of Nb, Ta and Fe substituting for Ti in the rutile, with Nb+Ta=2Fe. This follows the general formula for Nb-Ta rubles of Fe_x(Nb,Ta)_{2x}Ti_{1-3x}O₂ (Klein and Hurlbut, 1993).

Sample	R1	R6	R11	G6
Number %				
columbite/tantalite	18	34	16	17
rutile	22	33	33	8
topaz	44	23	24	61
cassiterite	8	4	6	1
apatite	3	2	14	14
Zircon	2	1	5	<1
monazite	<2	<1	<1	<1
others	<2	2	2	<1

Table 3. Mineral proportions in the accessory mineral concentrates.

Sample mineral %	R1 col	R1 col	R1 col	G6 col	G6 col	R6 col	R1 tan	R1 tan
Nb ₂ O ₅	69.41	51.42	70.45	33.47	45.17	52.20	23.90	28.42
Ta ₂ O ₅	6.71	30.22	6.91	48.51	35.67	27.65	58.98	54.33
TiO ₂	4.46	1.20	3.97	1.58	1.98	1.84	1.43	2.75
Sc ₂ O ₃	nd	nd	nd	nd	0.69	0.40	nd	nd
FeO	8.35	4.37	9.73	9.65	11.90	14.60	5.95	11.95
MnO	10.82	13.42	8.95	6.47	4.06	3.21	9.41	3.27
Total	99.75	100.63	100.01	99.68	99.47	99.90	99.66	100.72
Formula								
Nb	1.778	1.461	1.803	1.047	1.324	1.474	0.789	0.897
Ta	0.103	0.517	0.106	0.913	0.629	0.470	1.170	1.031
Ti	0.190	0.057	0.169	0.082	0.097	0.087	0.079	0.144
Sc	-	-	-	-	0.039	0.022	-	-
Fe ₂ *	0.396	0.230	0.461	0.558	0.645	0.763	0.363	0.698
Mn	0.519	0.714	0.429	0.379	0.223	0.170	0.582	0.193
cations	2.986	2.979	2.968	2.979	2.957	2.986	2.982	2.963
oxygens	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Sample mineral	R1 rut	R6 rut	R6 rut	R1 ilm				
Nb ₂ O ₅	15.68	14.90	18.42	23.58	14.05	15.58	6.96	nd
Ta ₂ O ₅	14.05	4.21	3.33	5.39	18.77	4.03	5.87	nd
TiO ₂	64.61	75.79	73.1	63.95	58.76	75.30	83.91	53.86
Sc ₂ O ₃	nd							
FeO	6.23	4.68	5.14	7.29	7.35	4.41	2.08	39.26
MnO	nd	nd	nd	nd	nd	rid	nd	6.70
Total	100.57	99.58	99.99	100.21	98.93	99.32	98.82	99.82
Formula								
Nb	0.109	0.098	0.121	0.161	0.103	0.103	0.045	-
Ta	0.059	0.017	0.013	0.022	0.083	0.016	0.023	-
Ti	0.750	0.828	0.801	0.725	0.718	0.825	0.903	1.017
Sc	-	-	-	-	-	-	-	-
Fe ₂ ⁺	0.080	0.057	0.063	0.092	0.100	0.054	0.025	0.824
Mn	-	-	-	-	-	-	-	0.143
cations	0.998	1.000	0.998	1.000	1.004	0.998	0.996	1.984
oxygens	2.000	2.000	2.000	2.000	2.000	2.000	2.000	3.000

Table 4. Representative microanalysis of columbite-tantalite, rattle and Mn-ilmenite.

The data show Nb_{0.01-0.18}, Ta_{0-0.13}, and Fe_{0.02-0.12} atoms per formula unit. Si, Sn, W and Al, reported in the ilmenorutile analyses from the topaz granites in Manning and Hill (1990), are not present. The ilmenite (Table 4) is manganiferous.

The relationships between the chemistry of the columbitetantalite and rutile are illustrated in Figure 8. As expected, there is a distinct separation between the two minerals. The Nb/Ta variation in the columbite-tantalite occurs with a minor variation in Ti, which is independent of the Nb/Ta ratio. There is an indication that two trends, one towards increasing Nb enrichment and one with Nb-Ta enrichment, are shown by the rutile data (Figure 8a). The clear trend shown by each mineral in the direction of the other (Figure 8b), can be explained in terms of limited solid solution between the phases. One interpretation is that simultaneous crystallisation of both minerals took place on a pseudo-binary solid solvus, with the extent of solid solution varying with temperature, presumably decreasing as the temperature is lowered. A similar interpretation has been placed on co-existing columbite-tantalite and rutile in pegmatites (Cerny *et al.*, 1986), and is consistent with the observation of there being inclusions of each mineral found within the other in the present grains. The chemical variations in these two minerals may show also that some fractionation within the topaz granite magma occurred at an early stage of cooling when the minerals rich in the incompatible elements Ti, Nb and Ta, were crystallising.

The monazite (Table 5) is the Ce-rich variety (monazite-(Ce) (Chang *et al.*, 1996). Two distinct types are present, the more common containing Th (0.07-0.09 atoms per formula unit) and in some cases minor Si. There is no variation in the ratios of the different

Sample %	R1	R1	R1	R1	R1	G6
SiO ₂	nd	nd	nd	0.73	nd	nd
ThO ₂	9.17	8.85	nd	9.57	9.17	nd
Ce ₂ O ₃	29.32	29.21	33.73	28.49	28.67	37.72
La ₂ O ₃	12.55	13.21	18.84	13.95	14.31	17.46
Nd ₂ O ₃	12.75	13.13	11.26	12.00	11.97	12.47
Pr ₂ O ₃	3.35	2.27	3.84	3.12	2.80	3.86
Sm ₂ O ₃	1.84	1.26	nd	1.41	1.96	nd
P ₂ O ₅	28.88	29.04	29.12	29.41	28.81	29.78
CaO	1.37	1.43	0.64	1.52	1.38	nd
Total	99.23	98.40	97.43	100.20	99.07	101.29
Formula						
Si	-	-	-	0.029	-	-
Th	0.084	0.081	-	0.086	0.084	-
Ce	0.412	0.431	0.497	0.409	0.423	0.541
La	0.186	0.196	0.280	0.202	0.213	0.252
Nd	0.183	0.189	0.162	0.168	0.172	0.174
Pr	0.049	0.033	0.056	0.045	0.041	0.055
Sm	0.026	0.018	-	0.019	0.027	-
P	0.984	0.990	0.992	0.977	0.983	0.987
Ca	0.059	0.062	0.028	0.064	0.060	-
cations	2.003	2.000	2.014	1.999	2.003	2.009
oxygen	4.000	4.000	4.000	4.000	4.000	4.000

Table 5. Representative microanalysis of monazite.

rare earth elements (REE). The second type contains no detectable Th, and has increased Ce and La (Figure 9). REE, other than La, Ce, Pr, Nd and Sm, were not detected in either type. Cassiterite, zircon, topaz and apatite show no significant variation in their chemistry or detectable elements (eg. Nb or Ta in cassiterite; Hf, Th or U in zircon; REE in apatite) other than the essential ones.

DISCUSSION

The mineral assemblage of columbite-tantalite, rutile, cassiterite and apatite is consistent within and between the two china clay pits. Major differences, which might occur if there were much heterogeneity in the topaz granite, are not present. The minerals, therefore, can be taken to be representative of the high specific gravity phases, which include most of the accessory minerals, in partially and completely kaolinized topaz granite. The minerals have been liberated during the kaolinization process, becoming concentrated during extraction and processing into the waste hydrocyclone underflow stream prior to further concentration in the laboratory. Small crystals and crushed fragments of dense minerals, such as cassiterite and wolframite from areas of mineralization in the granite, would become mixed in with the topaz and accessory minerals during extraction of the china clay. The cassiterite grains here might arise from areas of mineralization; but the absence of wolframite, linked with the consistent amounts of cassiterite in the samples, and the lack of significant Sn mineralisation in these china clay pits, does point to the cassiterite being an accessory phase forming during magmatic crystallization and disseminated throughout the topaz granite, rather than related to later vein-type mineralization events. A similar conclusion was drawn by Cuney *et al.* (1992) for cassiterite in the Variscan Beauvoir granite, France. They argued that Sn (and W) were retained in the magma until the end of crystallisation and were not partitioned significantly into an aqueous fluid. The Fe oxides, pyrite and sphalerite, found as rare grains in the heavy mineral concentrates, might come from a mineralization event, possibly cross-course mineralization, which is found in Rostowrack pit.

The presence of crystals with well developed morphologies for most of the major phases suggests that these minerals remain largely unaltered during the kaolinization process. The columbite-tantalite, however, shows some corrosion, indicating minor dissolution. Uraninite is present as an accessory phase in the topaz granite (Manning *et al.*, 1996). Its absence in the present samples, other than as a rare inclusion in columbite, would confirm a view that uranium is mobilised during kaolinization. The occurrence of monazite without Th might similarly be explained.

There are similarities between the assemblage described here and the accessory minerals found in evolved granites elsewhere, which are variously described as lepidolite or albite granites. In the past, these granites including the Nb-Ta accessory and other minerals, and any associated rare metal pegmatites have been considered to be metasomatic. However, following the discovery of volcanic and subvolcanic equivalents, they are now regarded as the products of magmatic crystallisation (see discussion in Helba *et al.*, 1997). One granite with close similarities to the St Austell granite is the Yichun Stock, China, (Schwartz, 1992). It comprises a biotite granite, grading upwards to a muscovite granite and lepidolite granite, the latter being the most evolved (cf. St Austell topaz granite). A diverse magmatic accessory assemblage of amblygonite/montebrazite, apatite, fluorite, Ta-Mn-columbite, Tammicrolite, Ta-cassiterite, ilmenite, monazite, zircon, beryl, pyrite and sphalerite with essential topaz are present in the lepidolite granite. The Nuweibi albite granite, Egypt (Helba *et al.*, 1997) contains accessory zircon, garnet, topaz, thorite, beryl, columbite-tantalite, microlite, ixiolite, stibio-tantalite and cassiterite. The Beauvoir topaz albite lepidolite granite (Massif Central, France) (Cuney *et al.*, 1992) also has similarities to the St Austell topaz granite and contains topaz, apatite, zircon, amblygonite, cassiterite, microlite, columbite-tantalite, uraninite, ruffe and sphalerite as magmatic accessory minerals. Comparison also can be made with the Younger Granites in Nigeria (Jacobson *et al.*, 1958), which are considered the source for alluvial cassiterite deposits. The more evolved albite-rich 'deuteric' granites contain the most abundant Nb minerals. Further similarities exist with pegmatites associated with leucogranites, such as the Greer Lake pegmatitic granite, Canada (Cerny *et al.*, 1986), which has columbite-tantalite, ixiolite, wodginite, Nb-Ta-rutile, cassiterite, microlite and ilmenite.

The granites and pegmatites mentioned above are considered to have potential or are actual sources of Nb, Ta and Sn, and it is significant that the geochemical data for the St Austell topaz granite show similar amounts of these elements. The Yichun lepidolite granite is mined for Ta and Li (Schwartz, 1992). The Nuweibi granite is said to contain 30 x 10⁶ tonnes (t) of NbTa ore reserves at 0.02% Ta₂O₅ and 0.01% Nb₂O (Helba *et al.* 1997). Sn and Ta are by-products from extraction of the kaolinized Beauvoir granite, and the research of Cerny *et al.* (1986) on the Greer Lake pegmatitic granite was supported in part by mineral exploration companies. At St Austell, assuming complete recovery, the trace element data in Table 2 indicate around 38t Nb, 30t Ta and 22t Sn (the latter using data of Manning and Hill, 1990) per million tonnes of granite. This is approximately equivalent to around 150,000t of china clay product, which is of the order of one years production for a medium sized china clay pit. The quantities of Nb, Ta and Sn are quite small, but the three metals have high intrinsic values. The columbite-tantalite, rutile and cassiterite are already released from the granite, are partially concentrated during china clay processing, and their high densities make further upgrading using gravity concentration a relatively straightforward procedure.

The major potential source for Nb, Ta and Sn must be within the large tailings dams in the St Austell area. These are the final repository for all of the fine waste from the china clay processing, and given the extraction rate of china clay within the topaz granite alone the tailings dams must contain at least several thousand tonnes of each of these metals. Unfortunately, the tailings dams also contain the waste from kaolinized lithium mica granite and tourmaline granite areas which have different accessory mineral assemblages. Thus, Nb, Ta and Sn are likely to be diluted, compared with what is available just from the topaz granite. However, lithium also is considered to be a potential by-product from china clay production (Hawkes *et al.*, 1987), and the tailings dams also contain major amounts of Li-mica. A strategy involving concentrating Li-mica by flotation, along with separation of Nb, Ta and Sn minerals by gravity processing should receive further consideration as a way of obtaining additional value from past and present china clay extractive operations in Cornwall.

ACKNOWLEDGEMENTS

This work forms part of a larger study of waste materials from china clay extraction, and is funded by a research grant from Goonvean Ltd to the first two authors. We acknowledge A.J. Clarke's assistance in making the mineral separations. The chemical analyses were made by Fiona Thomas. A.S. Ball is thanked for assistance with the scanning electron microscopy, and S. Pendray and J. Curnow for making the polished blocks.

REFERENCES

- BRISTOW, C.M. and EXLEY, C.S. 1994. Historical and geological aspects of the china clay industry of South-west England. *Transactions of the Royal Geological Society of Cornwall*, **21**, 247-314.
- CERNY, P., GOAD, B.E., HAWTHORNE, F.C. and CHAPMAN, R. 1986. Fractionation trends of the Nb- and Ta-bearing oxide minerals in the Greer Lake pegmatite granite and its pegmatoid aureole, southeastern Manitoba. *American Mineralogist*, **71**, 501-517.
- CHANG, L.L.Y., HOWIE, R.A. and ZUSSMAN, J. 1996. *Rock forming minerals, Volume 5B: non-silicates: sulphates, carbonates, phosphates, halides*. Longman, 383pp.
- CUNEY, M., MARIGNAC, C. and WEISBROD, A. 1992. The Beauvoir topaz-lepidolite albite granite (Massif Central, France): the disseminated magmatic Sn-Li-Ta-Nb-Be mineralization. *Economic Geology*, **87**, 1766-1794.
- EXLEY, C.S. and STONE, M. 1982. Petrology of the granites and minor intrusions. Pp 293-302, in Sutherland, D.S., *Igneous rocks of the British Isles*. John Wiley and Sons, 645pp.
- HAWKES, J.R., HARRIS, P.M., DANGERHELD, J., STRONG, G.E., DAVIS, A.E., NANCARROW, P.H.A., FRANCIS, A.D. and SMALE, C.V. 1987. The lithium potential of the St Austell Granite. *Report British Geological Survey*, **19**, No. 4.
- HELBA, H., TRUMBULL, R.B., MORTEANI, G., KHALIL, S.O. and ARSLAN, A. 1997. Geochemical and petrographic studies of Ta mineralization in the Nuweibi albite granite complex, Eastern Desert, Egypt. *Mineralium Deposita*, **32**, 164-179.
- HILL, P.I. and MANNING, D.A.C. 1987. Multiple intrusions and pervasive hydrothermal alteration in the St Austell Granite, Cornwall. *Proceedings of the Ussher Society*, **6**, 447-453.
- JACOBSON, R.R.E., MACLEOD, W.N. and BLACK, R. 1958. *Ring-complexes in the younger granite province of Northern Nigeria*. Geological Society of London, Memoir No. 1, 72pp.
- KLEIN, C. and HURLBUT, C.S. 1993. *Manual of mineralogy*. John Wiley and Sons, Inc, New York, 681pp.
- MANNING, D.A.C. and EXLEY, C.S. 1984. The origins of late-stage rocks in the St Austell granite - a reinterpretation. *Journal of the Geological Society*, **141**, 581-591.
- MANNING, D.A.C. and HILL, P.I. 1990. The petrogenetic and metallogenetic significance of topaz granite from the southwest England orefield. *Geological Society of America, Special Paper*, **246**, 51-69.
- MANNING, D.A.C., HILL, P.I. and HOWE, J.H. 1996. Primary lithological variation in the kaolinized St Austell Granite, Cornwall, England. *Journal of the Geological Society*, **153**, 827-838.
- SCHWARTZ, M.O. 1992. Geochemical criteria for distinguishing magmatic and metasomatic albite-enrichment in granitoids - examples from the Ta-Li granite Yichun (China) and the Sn-W deposit Tikus (Indonesia). *Mineralium Deposita*, **27**, 101-108.