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A preliminary report on the mineralogy
of the Tundulu and Songwe carbonatite
complexes, Malawi.

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INTRODUCTION.

A group of samples from the Tundulu and Songwe carbonatite complexes in Malawi, supplied by Dr. Appleton, have been studied by various mineralogical techniques. The aim was to characterise them and assess their usefulness as direct application fertilizers and sources of rare earth metals. A brief summary of the results obtained so far is given here and a full report will be made when the work is complete.

Polished thin sections were made from 17 samples. These were examined on the optical microscope and 7 were analysed on the electron microprobe. This examination showed that there were three main rock types, apatite rocks, ferruginous carbonatites and calcite carbonatites (sovitites) and the following report discusses them under these broad headings.

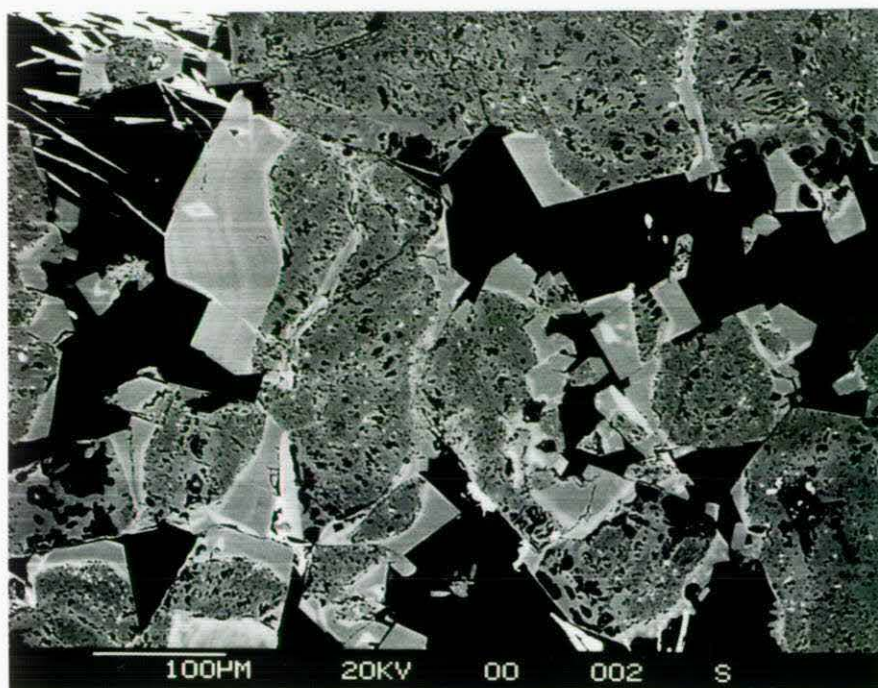
APATITE ROCKS.

Petrography.

The apatite rocks consist largely of a framework of apatite crystals, that constitute upwards of 75% of the rock, with various interstitial minerals. The most abundant interstitial mineral by far, is quartz, with carbonate being the only other mineral in significant amounts. The carbonate is usually a clear calcite but some rocks also have dark ferruginous carbonate that may have a rhomboidal shape. These large grains often have inclusions of apatite.

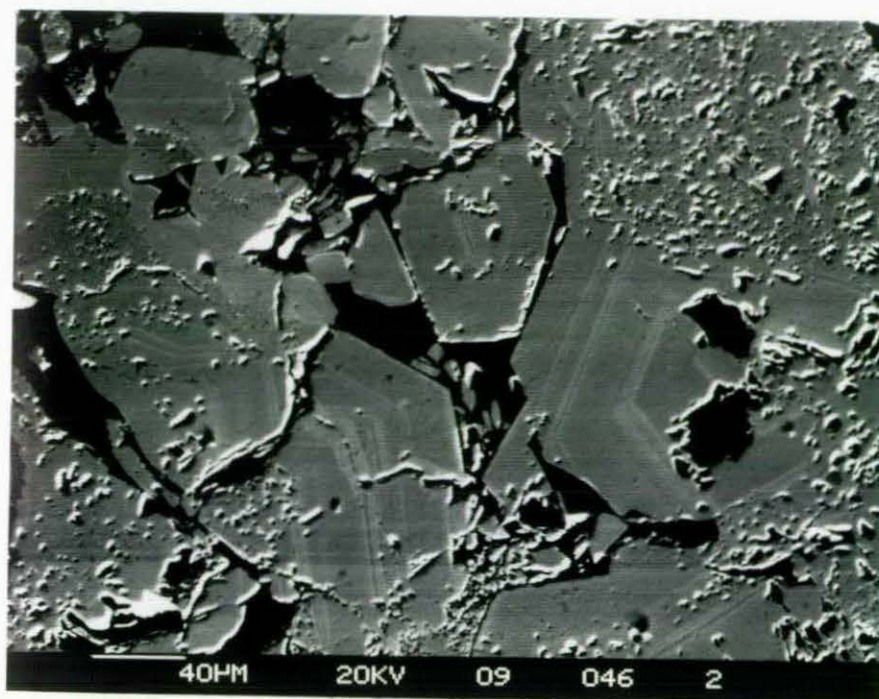
The apatite grains are generally around 100-300 microns in size. They are most unusual in that most of the grain is dark, full of tiny dark inclusions but around the margins is a clear rim that forms euhedral faces. The relative thickness of the rims varies considerably from one specimen to another, in sample T-142 they are up to about 50 microns while in T-160 they can be over 100 microns. One of the specific aims of the study was to try to ascertain what if any differences there were between the cores and rims of the apatite grains.

Two specimens T-142 and T-160 were studied on the scanning electron microscope using a backscattered electron detector which added greatly to the information gained from optical examination. T-142, Figs. 1&2 shows clearly the turbid cores with numerous small cavities caused by removal of material during the polishing process. The only elements other than those of apatite that was detected in the cavities was iron, suggesting that the cavities might originally be filled with goethite causing the dark colour in the thin sections when viewed in transmitted light. The outline of the cores is also significant. They are all rounded and in some cases embayed rather than the euhedral shape typical of apatite. This suggests that the original apatites were subjected to some kind of dissolution attack. The rims

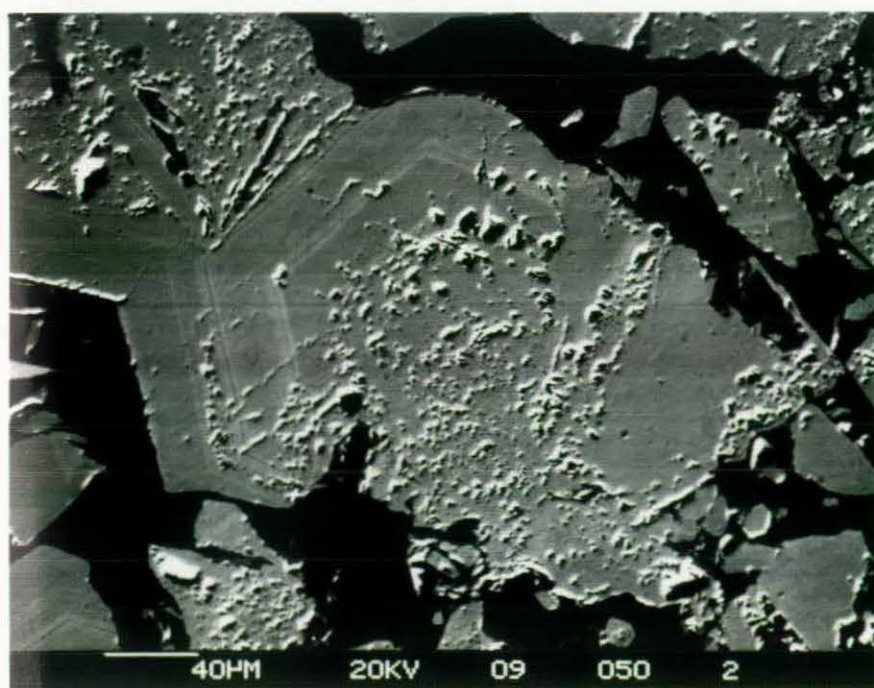


FIGS. 1&2. BACKSCATTERED ELECTRON PHOTOMICROGRAPHS OF APATITE ROCK T-142. CORRODED CORES AND EUHEDRAL, ZONED RIMS CLEARLY SHOWN. BLACK AREAS QUARTZ, WHITE NEEDLES SYNCHISITE.





FIGS 3 & 4. BACKSCATTERED ELECTRON PHOTOMICROGRAPHS OF APATITE ROCK T-159. CORRODED CORES AND EUHEDRAL ZONED RIMS.



show clearly the euhedral shape with well formed crystal faces and also that there is fine scale zoning. There is a suggestion that the rims are slightly brighter than the cores indicating that they have a slightly higher mean atomic number. It is clear that certain zones and patches are significantly brighter and indicates compositional variation. T-160, Figs.3&4 shows broadly similar features but with wider rims and much less marked compositional variation. The optical and SEM study shows two distinct phases of apatite formation, an early phase followed by dissolution and then precipitation with fine zoning and lack of reequilibration suggesting relatively low temperatures, possibly in a hydrothermal environment.

The interstitial parts of the rock contain a number of accessory minerals in addition to the quartz and calcite. The most prominent of these are the rare earth minerals that occur as sheaves of yellowish to dark brown needles. Individual needles are up to around 100 microns in length and 20 microns in diameter but usually smaller than this, giving sheaves around 300-500 microns across. Pyrochlore and rutile are present in most rocks and in some samples pyrite.

Microprobe Study.

Apatite grains were analysed from all the apatite rocks and the results are given in Tables 1-5. In general both the turbid core and the clear rim were analysed for each grain but in sample T-160 where the clear rims are particularly broad and zoned a series of points across the rim of one grain was analysed.

The ionic formulae given in the Tables are calculated on the basis of 10 cations in the Ca sites as elements such as F and C(CO₃) are not detected and the exact number of oxygen equivalents is not known. All the tables contain a row of figures labelled X/6-x, the ratio used by McClellan and Gremillion (1980) as an indicator of the amount of carbonate substitution for phosphorus, in a generalised formula for carbonate apatite:



The x in the ratio is the proportion of CO₃ but as this has not been determined it is assumed that all the deficiency in the P sites is due to CO₃ hence x is actually 6-P and 6-x is P.

All the apatite spectra showed the presence of F but the peak is too small to make any quantitative estimate.

The apatite analyses in the tables show a number of general features. Firstly there is a general correlation between the Na content of the apatites and the deficiency in the P sites. This is clearly shown in Fig 5. This is the coupled substitution of Na for Ca and CO₃ for PO₄ in fluorapatite forming a carbonate apatite or francolite component. Another feature clear on both the Figure and the tables is that the rims have a higher francolite component than the cores. Also clear from the tables is that some samples, e.g. T-144 have generally higher proportions of francolite in both cores and rims than

APATITES

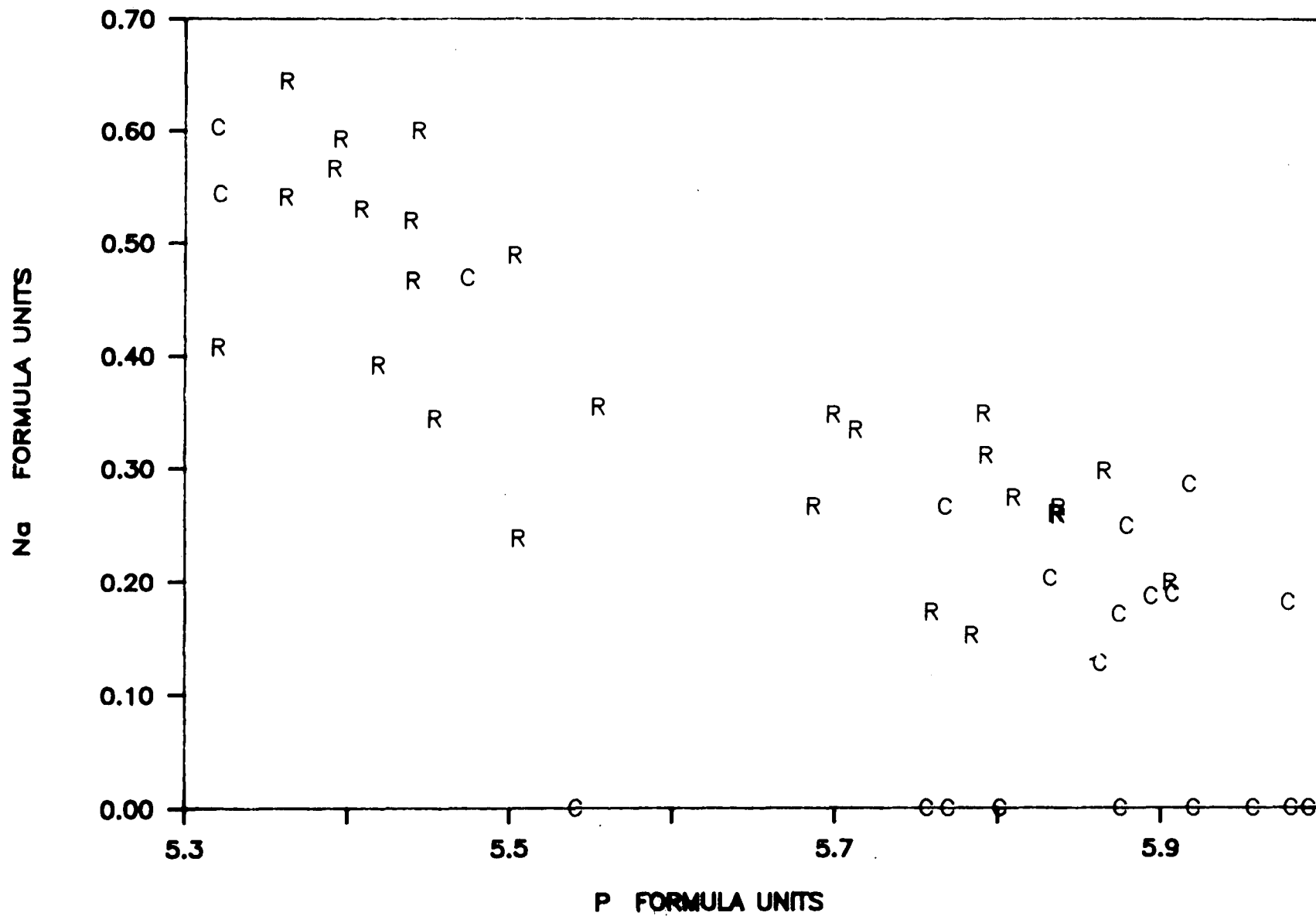
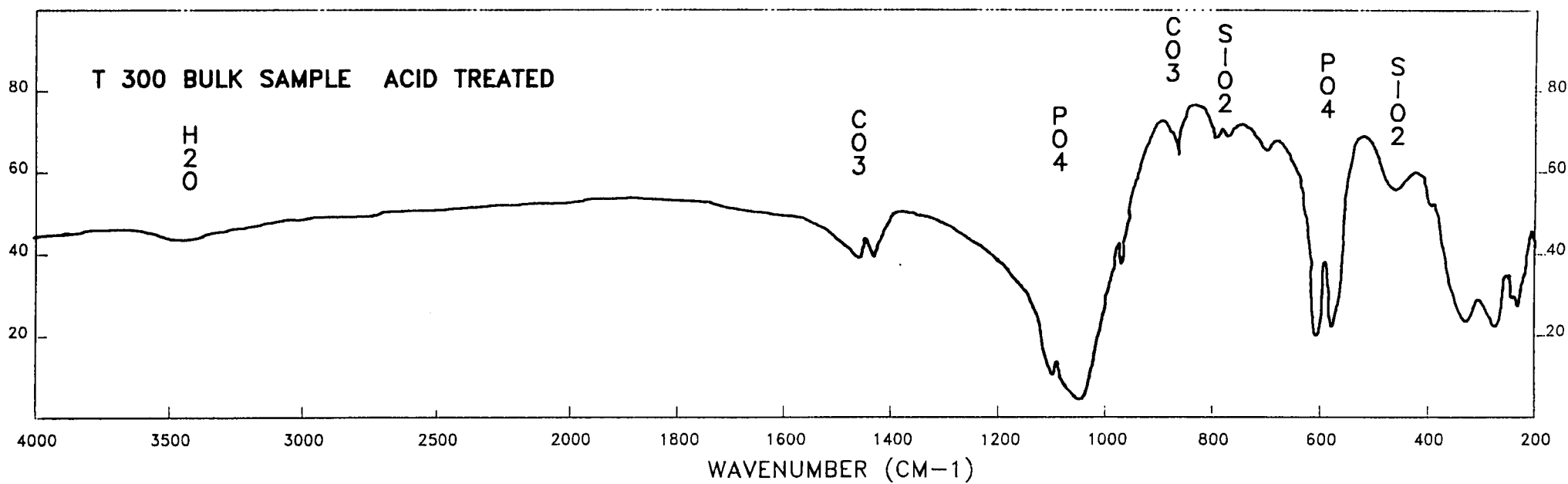
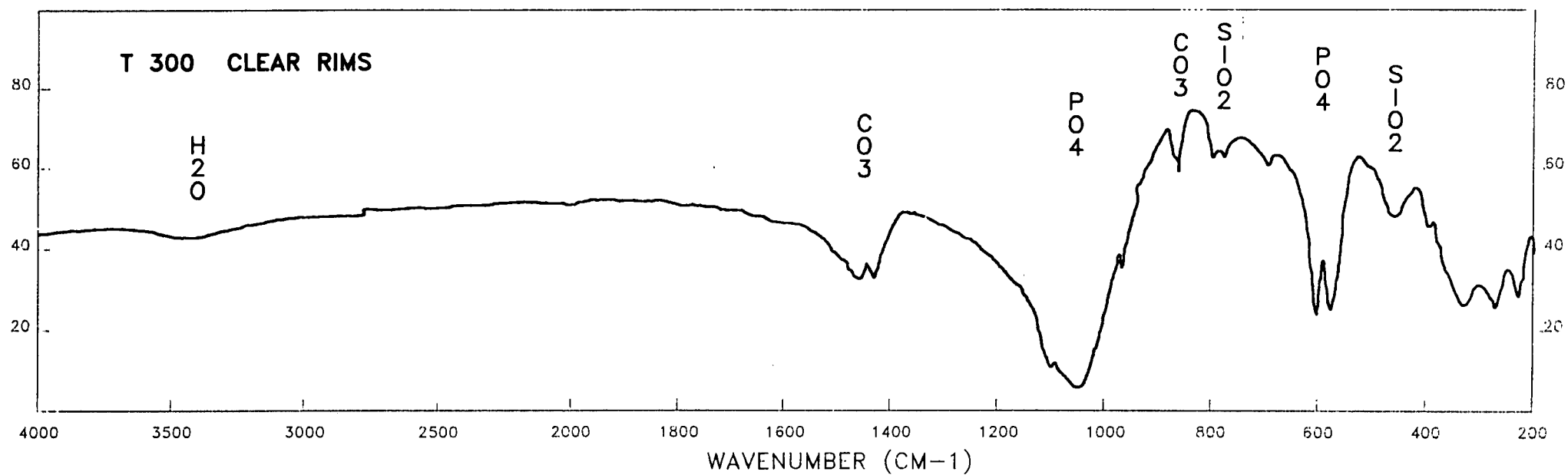


FIG. 5. Na v P for apatites. C-centre, R-rim.

FIG. 6.



most of the other samples. The general pattern is that the francolite component is relatively low in the cores of the grains, $x/6-x$ around 0.02-0.03 but higher in the rims up to 0.1 with a maximum of 0.13. The maximum substitution of CO_3 in an ideal francolite gives a value around 0.3.

The tables show very variable amounts of Sr and Y and no consistent pattern of the distribution of these elements has yet emerged.

Infra-red Spectrometry.

An apatite concentrate T-300 had been made from one of the apatite rocks by Mr Briggs. Various subsamples of T-300 have been studied on the infra-red spectrometer by Mr Bland, in an attempt to further classify the apatite types and confirm the differences between cores and rims inferred from the microprobe analyses.

Fractions were obtained by hand picking under a binocular microscope to give a clear fraction representative of the rims and one white and one yellowish turbid fraction representing the cores. An unsorted fraction was treated with 10% acetic acid to make sure any carbonate peaks were not due to calcite contamination. All fractions gave similar traces. (see Fig 6) with large peaks for PO_4 and smaller peaks for CO_3 and SiO_2 and a broad peak for H_2O . The H_2O peak is due to adsorbed water from the atmosphere and there is not a sharp OH peak due to hydroxyl in the apatite lattice. The SiO_2 is presumably due to small inclusions of quartz in the apatite grains. The size of the CO_3 peak is not significantly altered by acid treatment and it is therefore thought to be due to a carbonate substitution in the apatite structure. The CO_2 index of McClellan and Gremillion (1980) has been calculated and also a rough estimate of the CO_2 content has been made by comparison with a trace of a previously analysed carbonate apatite.

	CO_2 Index	% CO_2
Clear apatite	0.40	4
White turbid	0.22	3
Yellow turbid	0.29	3
Acid treated bulk	0.24	2

The CO_2 index is on a scale of 0-1, compared to the $x/6-x$ index which is from 0-0.3 for the same range of substitution so there is a rough correlation between the two values for the rims, i.e. around 35% of the possible carbonate substitution. The infra red values for the cores suggest rather higher values than was estimated from the microprobe results.

X-Ray Diffraction Study.

The bulk sample T-300 has been examined on the diffractometer by Mr Kemp and Mr Bland has calculated the apatite cell parameters from this data, the results are:

a=9.3574 +/- 0.00168 angstroms
c=6.8893 +/- 0.0022 "

According to the data of McClellan and Gremillion this corresponds to a mole ratio $\text{CO}_3 : \text{PO}_4$ of 0.5- 0.1 (x/6-x). To check if there were discernible differences between the cores and rims by XRD methods Mr Nancarrow hand picked fractions of a few grains of the clear and turbid grains and examined them using the powder camera method. The results were:

white	turbid	clear
a=9.345 +/- 0.005		a=9.337 +/- 0.004
c=6.885 +/- 0.005		c=6.892 +/- 0.004

This shows that there is only a minimal difference between the two by this method as there is a slight overlap of errors but suggests that the rims have a smaller a cell dimension indicating a higher carbonate substitution consistent with the other data. The amount of substitution indicated is slightly higher than from the diffractometer around 0.18 but as this is a less accurate method the diffractometer figure is probably more reliable.

Summary of apatite data.

The analysis of apatites by three different methods indicate that there is no significant OH or Cl present but the CO_3 shows that there are essentially fluorapatites with a carbonate apatite component. This carbonate apatite component is probably approaching 0.1 mole substitution, about 30% of that possible. It is also clear that the rims have a higher proportion of carbonate present.

Rare earth minerals.

Many apatite rocks contain interstitial rare earth minerals and T-142 which was studied on the microprobe is a typical example. The main mineral present is the fluoro-carbonate synchisite-(Ce) and analyses are given in Table 6 cols. 1-3. They show 6 cations on the basis of 7.5 oxygens of which 3 are Ca, corresponding to an idealized formula of $\text{Ca}_3\text{Ce}_3(\text{CO}_3)_6\text{F}_6$ allowing for the elements C and F that are not detected. Analysis 4 has a low total but the formula is very similar to the others and is probably due to a poor surface polish. Analysis 5 has a completely different ratio of Ca to REE and is probably an intergrowth of synchisite and bastnaesite and this problem will be discussed in a later section. The chondrite normalized plots of the minerals all show similar patterns, with straight negative slopes due to enrichment in La and Ce.

The apatite rock T-159 contains rare earth minerals in a different form, the sheaf-like aggregates have mostly been altered to brown, very fine, granular patches. Analyses of these patches shows them to be of quite variable composition Table 7. Analyses 1-3 are a

T 142 REE MINERALS

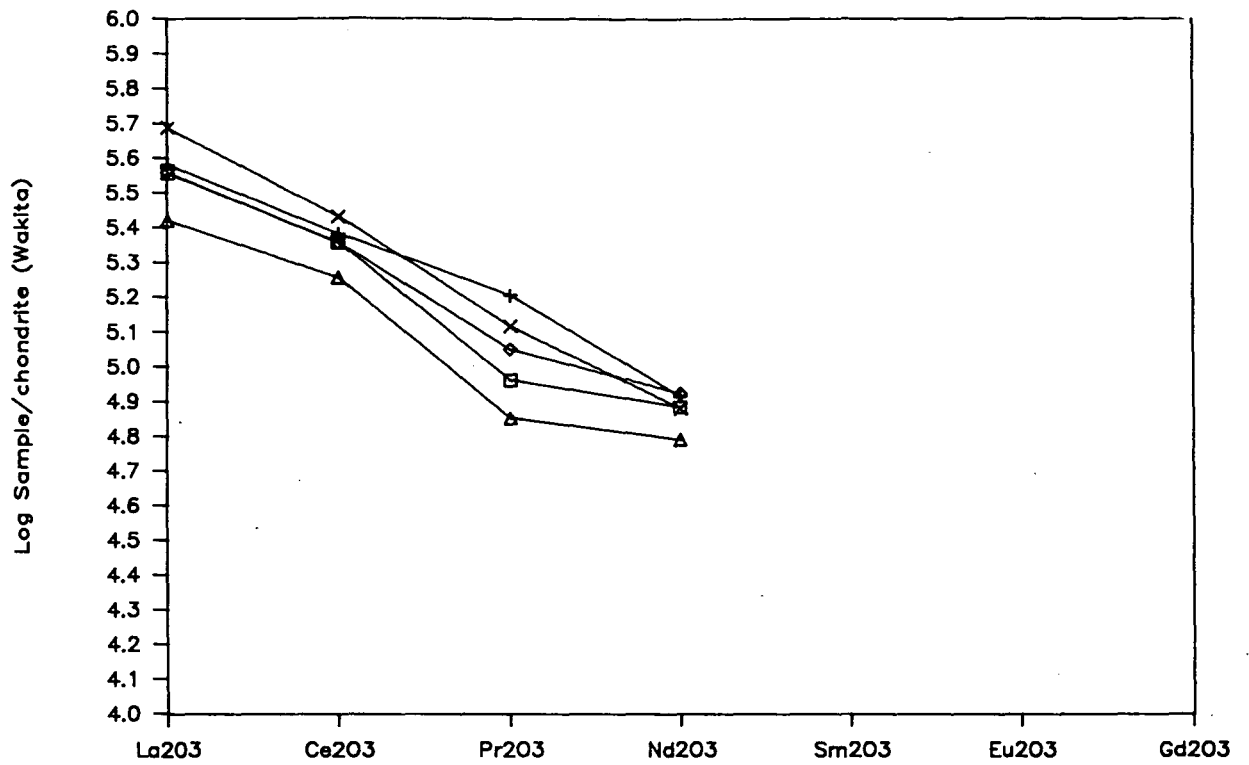


FIG. 7. SYNCHISITE.

T 159 REE MINERALS

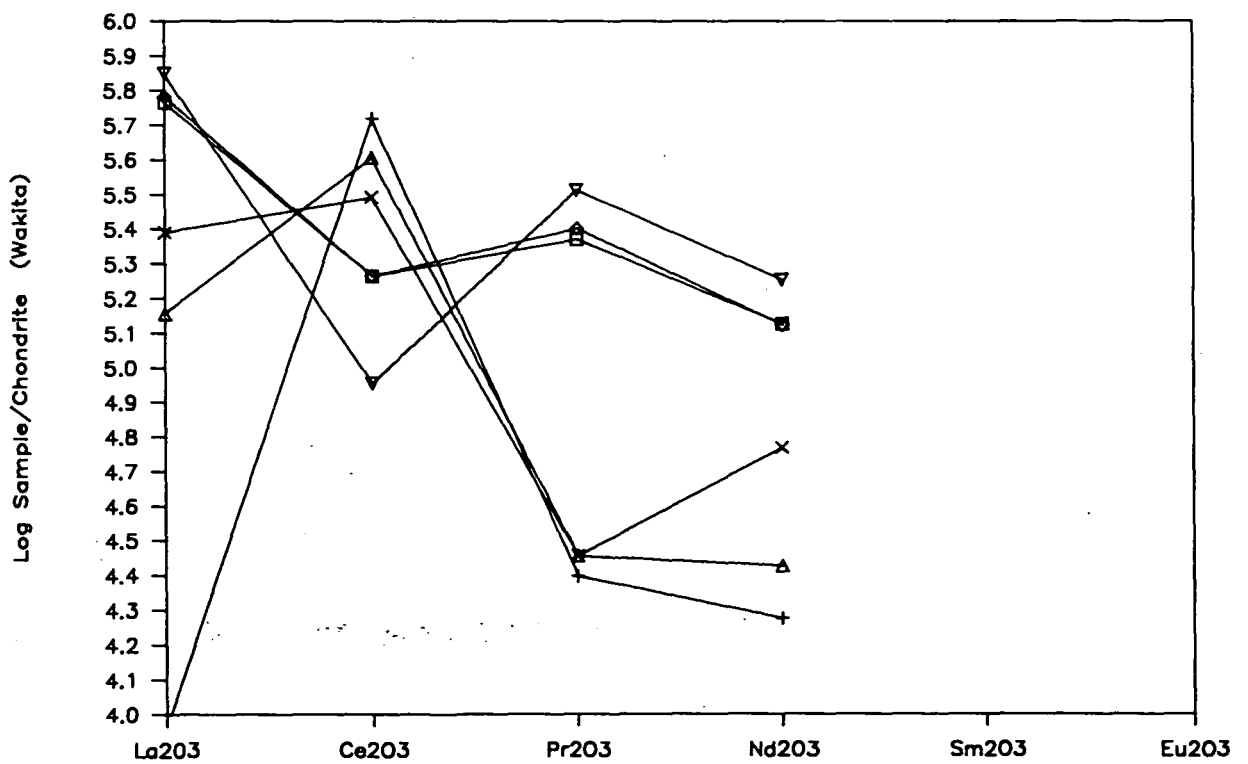


FIG. 8. RHABDOPHANE-(LA).

phosphate mineral and the totals around 90% show that it is hydrous and therefore rhabdophane. The content of La is higher than Ce and therefore should be called rhabdophane-(La). This is the only mineral type where this has been seen and the ratio is also variable. Other analyses within these brown areas gave high Ce contents and low La and variable amounts of P. This suggests that they are probably a mixture of a Ce-rich mineral and the rhabdophane-La, and the low totals suggest the Ce mineral has a large proportion of undetected elements, either a carbonate or fluoride. The chondrite normalized patterns Fig.8 are different from the typical bastnaesite-synchisite type. Analyses 1 and 2 (open squares and closed triangles) are the most similar but with a pronounced dip at Ce but possibly the most significant are the extreme compositions analyses 3 and 4 (inverted triangles and crosses). These indicate a marked departure from the group behavior of the rare earth elements and the formation of a separate Ce mineral. This has been observed previously by Styles and Young (1983), Adams (1968) and is thought to be due to the oxidation of Ce from 3+ to 4+ during alteration.

CALCITE CARBONATITES (SOVITES).

Petrography

The calcite carbonatites consist largely of coarse grained calcite that shows a marked shape fabric with elongate grains giving a foliation to the rock. The grains show a range of sizes up to 1cm but generally around 1mm. Some rocks are however quite fine grained, again with a marked foliation but often a mortar texture to the calcite indicating annealing probably due to the effects of deformation. The main accessory mineral is the ferruginous carbonate which is usually present in streaky layers and biotite and apatite are often present. All these minerals are elongate along the foliation. Very small amounts of feldspar, sphene, zircon, pyrochlore, bastnaesite or synchisite, perovskite and pyrite (partly to completely replaced by hematite) are also present. Several sovites have cross cutting veins of coarse clear calcite.

Microprobe Study.

Only one sample of the sovites, T-152, has been analysed on the microprobe. The carbonate is calcite, with around 1 wt % of FeO and MnO, up to 0.5% MgO and the highest impurity is SrO between 1.5-2%. This high Sr content is in agreement with the bulk chemical analyses where around 15,000 ppm was found in other sovites. The apatites in this rock has a high phosphorus and low Na indicating very little carbonate apatite substitution compared with the apatite rocks, less than 0.01. The feldspars are a potassic K-feldspar with composition Or88.5 Ab11.5. The biotites have high TiO₂ contents

around 4wt% and have Mg/Mg+Fe around 0.5. Many of the dark brown minerals are TiO₂, probably rutile, but in some areas they are associated with TiFe oxides suggesting some of them are formed at the expense of earlier ilmenite.

FERRUGINOUS CARBONATITES.

Petrography.

This group covers quite a diverse group of rocks but all having the common feature that they contain substantial amounts of a ferruginous carbonate that gives a dark brown appearance to the thin sections. In some ways they have textural affinities with the apatite rocks, in that many consist of an early formed framework, in this case of the dark carbonate, with interstitial areas filled with various minerals. The commonest interstitial mineral is a clear calcite but in some quartz is quite abundant and most have the rare earth minerals, bastnaesite-synchisite etc. Apatite can be abundant in some rocks, e.g. T-155, and there is possibly some kind of transitional relationship to the apatite rocks. The apatite is usually intergrown with the carbonate as inclusions within the larger carbonate crystals. The carbonate can take on several forms, as large plates, irregular masses or colloform structures.

Microprobe Study.

Two samples, T-153 and T-155 have been analysed on the electron microprobe. Determining the exact nature of the dark carbonate material proved very difficult as results were very variable. The examination in reflected light showed that there was abundant goethitic material within these dark areas and most analyses showed that they consisted of calcite with fine Fe and Fe-Mn phases. The proportions of Fe and Mn varied considerably from Fe dominant to Mn dominant though the latter are much rarer. They are assumed to be hydroxides but this has not been definitely proved. It is thought that these calcite goethite intergrowths are the replacement products of an original ferruginous carbonate. In a few places analyses were obtained that appear to be of the "original" carbonate and the results are given in Table 8, which shows the analyses, ionic formulae and theoretical carbonate end member molecules. Most of the dark carbonates have around 50-60% calcite, 20-30% siderite and variable amounts of magnesite, rhodochrosite and a little strontianite and witherite. The primary carbonate is essentially ankerite.

T-155 contained abundant apatite and analyses are given in Table , this shows that they have high P contents, low Na, indicating little carbonate substitution. This makes them similar to the cores of the apatites in the apatite rocks.

T-153 REE MINERALS

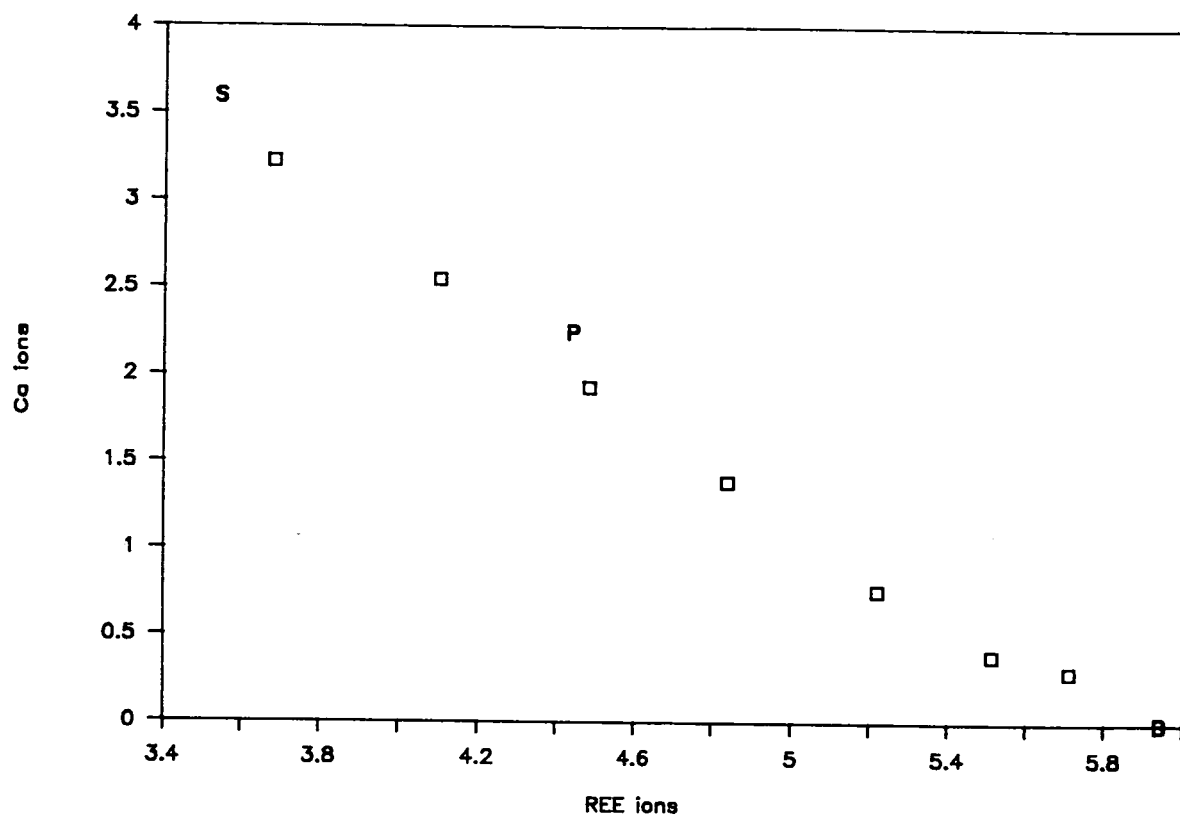


FIG. 9. Ca v Total REE for Bastnaesite-Synchisite intergrowths.

T 153 REE MINERALS

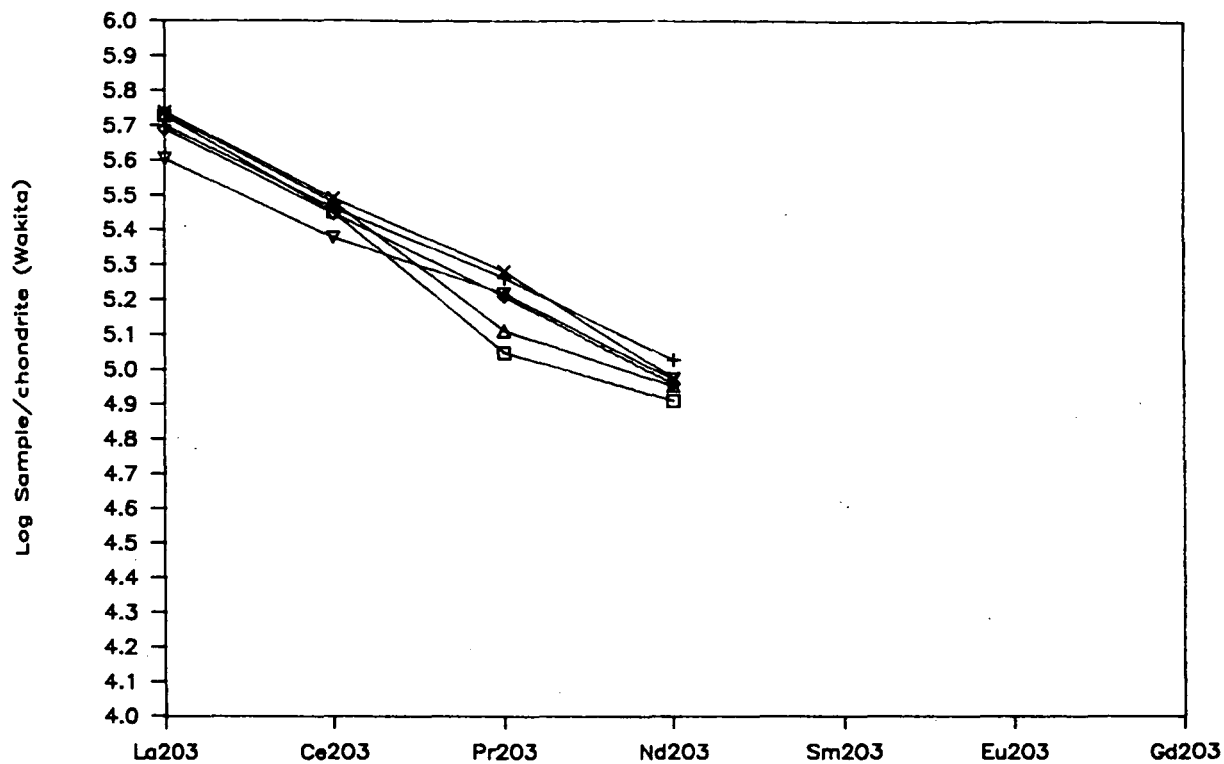


FIG. 10. BASTNAESITE-SYNCHISITE.

T 153 REE MINERALS/2

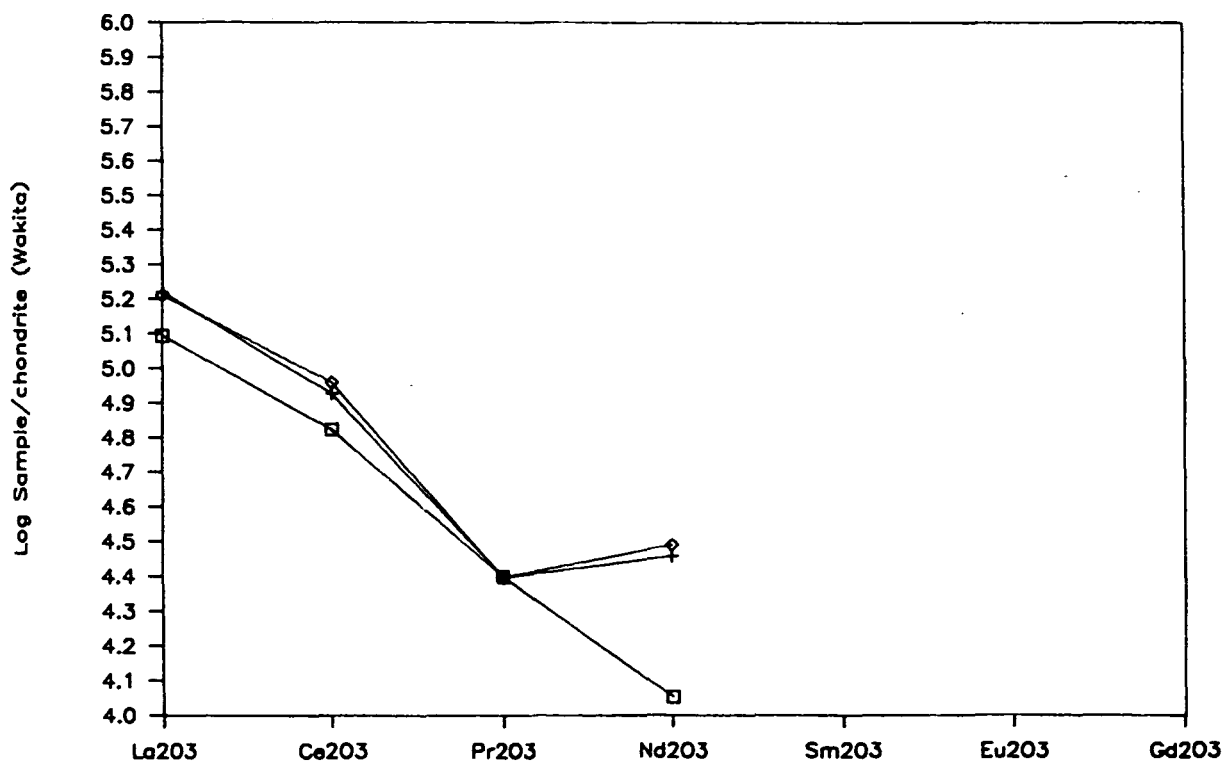


FIG. 11. FLORENCITE.

The ferruginous carbonatites often contain abundant REE minerals, particularly T-153. They usually occur as sheaves of brown needles and it was difficult to analyse individual needles as they are only a few microns in diameter. The analyses obtained are given in Table.10 and show that they have a wide range of Ca contents that span the compositions of bastnaesite, parisite and synchisite. In the Table the formula based on 9 oxygens would contain 6 cations, all REE for bastnaesite, 6.75 cations of which 4.5 are REE for parisite and 7.2 cations with 3.6 REE for synchisite.

The variation is shown diagrammatically in Fig. 9 , where B,P and S are theoretical compositions for bastnaesite, parisite and synchisite. Such a spread of compositions could be caused either by solid solution in a series between bastnaesite and synchisite or by fine intergrown mixtures that are finer than the electron beam. The minerals in question have different atomic structures and solid solution is unlikely and therefore they are thought to be mixtures. The chondrite normalized patterns Fig.10 show quite steep negative slopes indicating strong enrichment in La and Ce and relatively straight lines, similar to the synchisites in T 142. Rare earth elements were also found in brown featureless masses and veins usually within the interstitial parts of the rock. Analyses, Table 11, show that they contain abundant Al and P indicating that they are probably florencite, the rare earth rich member of the plumbogummite group. The formula on the basis of 11 oxygens agrees well with this showing 3Al, 2P and a total of 6 cations. The content of Sr is quite high indicating a substantial goyazite component. The analysis with high Ca does not give a good formula and indicates contamination by calcite rather than a crandallite component. The chondrite normalized patterns Fig 11 are similar to those from the bastnaesites etc. but with somewhat greater variability in Nd.

Summary of the rare earth mineral data.

A number of minerals containing rare earth elements in high concentrations have been found. The order of formation is "early" fluorocarbonates associated with interstitial quartz and calcite and later phosphate bearing minerals, such as florencite and rhabdophane by alteration of the fluorocarbonates. The fluorocarbonates are part of a late magmatic hydrothermal phase and the alteration is later and at much lower temperatures, possibly due to groundwater circulation.

The grain size of all the types of rare earth minerals is very small, usually only a few microns or less and even aggregates of the needle-like minerals only reach a few hundreds of microns. This would make separation of them by physical methods extremely difficult.

CONCLUSIONS.

The petrographic study of the thin sections revealed that the rocks had formed during several phases of crystallisation. The first phase formed the main framework of the rocks with the crystallisation of apatite in the apatite rocks and carbonates in the carbonatites. This was followed by a period of ?hydrothermal alteration during which the apatites were corroded and went turbid and dark and possibly the early formed ankeritic carbonates were altered. A second period of crystallisation followed with the formation of the clear rims on the apatites and the bulk of the interstitial minerals, calcite, quartz and the rare earth fluorocarbonates. This was clearly a fluid-rich environment, possibly a late magmatic stage and the apatite formed at this stage had a higher carbonate apatite component. Following this and at much lower temperatures was a groundwater or weathering type of alteration with further calcite veining and the formation of florencite and rhabdophane.

Mineralogical study of apatites, particularly to assess the carbonate-apatite component, shows that it is variable from one rock to another but in any rock is always higher in the clear rim than the turbid core. An average figure for the carbonate for phosphate substitution is around 10 mole % approx 30% of that possible. This is quite high for apatites from an igneous source but much lower than those from sedimentary phosphate deposits.

A study of the rare earth element content of the rocks showed that it is largely contained in the fluorocarbonates bastnaesite and synchisite. These occur as fine fibrous crystals only a few microns in size amongst the interstitial quartz and calcite. In some samples they have been altered to very fine granular patches of florencite and rhabdophane-(La) intergrown with an unidentified cerium mineral. The very fine grainsize of these minerals would make extraction by physical methods extremely difficult. Their occurrence as fluorocarbonates could make chemical extraction possible, though presence of large amounts of other carbonates in the rocks would create difficulties.

APPENDIX.

Analytical Techniques.

Mineral analyses were carried out using a Link Systems energy-dispersive X-ray analyser on a Cambridge Instruments Microscan 5 electron microprobe. Elements of atomic number 11(Na) and higher can be analysed quantitatively and the presence of substantial amounts of fluorine can be detected but not analysed for in a meaningful way. The limits of detection are usually around 0.2 wt% oxide but are higher if there are severe spectral interferences and may reach 1% in the worst case. The detection limits for the rare earth elements are around 0.35 wt% oxide. A description of the techniques used is given by Dunham and Wilkinson (1978) for common elements and Styles and Young (1983) for the rare earth elements.

Throughout the work an accelerating voltage of 15kV, a beam focused to approximately 4 microns and a specimen current around 5×10^{-9} amps was used.

The quality of the analysis of phosphorus is clearly crucial to the study of apatites as the deficiency in the P sites is used as an estimate of the carbonate substitution. Tests have been carried out on both the precision and accuracy of the P determination. To test the precision, repeated analyses were made of one very small area of the apatite standard used for calibration and the results are given in Table 12. This shows that concentrations found are very close to the given values, as is expected for the calibration standard. The standard deviations, showing the variation due to instrument parameters etc. are quite small, 0.40 Wt% for CaO and 0.25wt% for P₂O₅, indicating a relative error of 0.5-1%. Tests on the accuracy were made by making repeated analyses of two other apatite standards. The means of these analyses showed that one standard came out with a relative error which was 0.5% low and the other came out 1% high. The standard deviations were much the same as the previous test. The results are thus within the expected range of analytical error, particularly bearing in mind that there is rarely perfect agreement between mineral standards. The determinations of P therefore have accuracy and precision which is +or- 1% relative or about 0.4wt% P₂O₅.

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TABLE 1.

T 142 APATITES.

	1	2	3	4	5	6	7	8
CaO	53.90	53.73	54.17	52.95	53.77	52.47	54.38	53.47
Na ₂ O	0.63	0.47	0.58	1.07	0.39	1.75	0.00	0.52
SrO	0.60	0.00	0.00	0.76	0.46	0.50	0.00	0.00
Y ₂ O ₃	0.80	1.63	0.00	0.00	0.00	0.00	1.01	1.07
P ₂ O ₅	41.15	40.54	41.28	40.52	40.60	38.15	40.07	40.84
Total	97.08	96.36	96.03	95.28	95.22	92.87	95.46	95.90

Number of ions on the basis of 10(Ca+Na+Sr+Y)

Ca	9.668	9.702	9.811	9.577	9.827	9.386	9.909	9.732
Na	0.203	0.152	0.189	0.349	0.128	0.566	0.000	0.171
Sr	0.058	0.000	0.000	0.074	0.046	0.048	0.000	0.000
Y	0.071	0.146	0.000	0.000	0.000	0.000	0.091	0.097
P	5.832	5.784	5.907	5.791	5.862	5.391	5.769	5.874
x/6-x	0.03	0.04	0.02	0.04	0.02	0.11	0.04	0.02

- | | | |
|----|--------------------|---|
| 1. | AP1 C TURBID | C |
| 2. | AP1 E CLEAR | R |
| 3. | AP2 C TURBID | C |
| 4. | AP2 E CLEAR | R |
| 5. | AP3 C | C |
| 6. | AP4 E | R |
| 7. | AP5 C IN CLUSTER | C |
| 8. | AP6 C LARGE TURBID | C |

T 144 APATITES.

TABLE 2.

	1	2	3	4	5	6	7	8	9	10	11	12
CaO	53.54	53.86	53.18	53.98	52.98	51.86	51.73	51.77	53.09	53.23	53.75	53.71
Na ₂ O	0.00	1.22	1.07	0.00	0.95	1.87	1.83	1.43	0.82	1.71	0.00	0.74
SrO	0.66	0.61	0.48	0.90	0.95	0.55	0.47	0.49	0.96	0.87	0.49	0.75
Y ₂ O ₃	0.00	0.00	0.86	0.00	0.00	0.90	0.00	1.06	1.08	0.00	1.84	1.33
P ₂ O ₅	40.86	38.67	40.25	38.19	40.48	37.69	38.09	38.20	40.03	38.25	41.15	39.10
Total	95.05	94.36	95.85	93.08	95.37	92.86	92.12	92.94	95.99	94.06	97.23	95.63

Number of ions on the basis of 10 (Ca+Na+Sr+Y)

Ca	9.934	9.550	9.529	9.911	9.595	9.264	9.354	9.388	9.543	9.373	9.786	9.572
Na	0.000	0.391	0.348	0.000	0.312	0.603	0.600	0.469	0.266	0.544	0.000	0.237
Sr	0.066	0.059	0.047	0.089	0.093	0.053	0.046	0.048	0.094	0.083	0.048	0.073
Y	0.000	0.000	0.077	0.000	0.000	0.080	0.000	0.095	0.097	0.000	0.166	0.118
P	5.991	5.419	5.699	5.540	5.792	5.320	5.443	5.473	5.687	5.322	5.920	5.505
x/6-x	0.00	0.11	0.05	0.08	0.04	0.13	0.10	0.10	0.06	0.13	0.01	0.09

- | | | | | |
|-----|------|---|--------------|---|
| 1. | AP1 | C | TURBID | C |
| 2. | AP1 | E | CLEAR | R |
| 3. | AP2 | | SMALL CLEAR | R |
| 4. | AP3 | C | SMALL TURBID | C |
| 5. | AP3 | E | | R |
| 6. | AP4 | C | LARGE TURBID | C |
| 7. | AP4 | E | | R |
| 8. | AP5 | C | TURBID | C |
| 9. | AP5 | E | | R |
| 10. | AP 6 | C | IN CLUSTER | C |
| 11. | AP7 | C | IN CLUSTER | C |
| 12. | AP7 | E | | R |

T 159 APATITES

TABLE 3.

	1	2	3	4	5	6	7	8	9	10	11	12
CaO	54.43	53.18	54.43	53.29	53.49	52.04	53.91	52.64	52.88	54.83	53.21	52.96
Na ₂ O	0.00	0.60	0.00	1.04	0.88	0.89	0.55	0.81	0.83	0.58	0.53	0.79
SrO	0.00	0.35	0.36	0.84	0.72	0.00	0.00	0.56	0.96	0.00	0.97	0.88
Y ₂ O ₃	1.08	0.00	0.00	1.05	0.00	1.33	0.00	1.22	0.00	0.00	1.18	1.05
P ₂ O ₅	40.87	40.70	41.35	40.59	41.53	40.31	41.53	40.63	40.36	41.67	40.29	40.91
Total	96.37	94.83	96.14	96.82	96.62	94.57	95.99	95.86	95.03	97.08	96.18	96.60

Number of ions on the basis of 10 (Ca+Na+Sr+Y)

Ca	9.902	9.766	9.964	9.491	9.643	9.581	9.818	9.570	9.632	9.813	9.626	9.560
Na	0.000	0.199	0.000	0.335	0.286	0.298	0.182	0.265	0.274	0.187	0.173	0.259
Sr	0.000	0.035	0.036	0.081	0.070	0.000	0.000	0.055	0.094	0.000	0.095	0.086
Y	0.098	0.000	0.000	0.093	0.000	0.122	0.000	0.110	0.000	0.000	0.106	0.094
P	5.875	5.905	5.980	5.712	5.917	5.865	5.977	5.837	5.809	5.893	5.759	5.835
x/6-x	0.02	0.02	0.00	0.05	0.01	0.02	0.00	0.03	0.03	0.02	0.04	0.03

1.	AP1	C	TURBID	C
2.	AP1	E	CLEAR	R
3.	AP2	C	TURBID	C
4.	AP2	E	CLEAR	R
5.	AP3	C	TURBID	C
6.	AP3	E	CLEAR	R
7.	AP4	C	TURBID	C
8.	AP4	E	CLEAR	R
9.	AP5	CLEAR	SMALL	R
10.	AP6	C	TURBID	C
11.	AP6	E	CLEAR	R
12.	AP7	CLEAR	SMALL	R

T 160 ZONED APATITE

TABLE 4.

	1	2	3	4	5	6	7	8	9
CaO	54.09	54.69	52.83	50.77	53.67	53.07	52.54	54.10	52.33
Na2O	0.00	0.00	1.62	1.99	1.27	1.07	1.64	1.54	1.66
SrO	0.00	0.65	0.86	0.58	0.55	0.55	0.86	0.00	0.59
Y2O3	0.00	0.00	0.00	2.28	0.00	1.39	0.00	0.00	0.00
P2O5	41.62	40.10	38.69	37.88	37.88	38.64	38.31	39.60	37.77
Total	95.72	95.45	94.00	93.51	93.37	94.71	93.34	95.24	92.36

Number of ions on the basis of 10(Ca+Na+Sr+Y)

Ca	10.000	9.936	9.397	9.096	9.540	9.479	9.387	9.512	9.402
Na	0.000	0.000	0.520	0.644	0.407	0.344	0.530	0.488	0.541
Sr	0.000	0.064	0.083	0.057	0.053	0.053	0.083	0.000	0.058
Y	0.000	0.000	0.000	0.203	0.000	0.123	0.000	0.000	0.000
P	6.080	5.756	5.438	5.362	5.320	5.453	5.408	5.502	5.362
x/6-x	-0.01	0.04	0.10	0.12	0.13	0.10	0.11	0.09	0.12

1. CENTRE	C
2. "	C
3. INNER ZONE	R
4.	R
5.	R
6.	R
7.	R
8.	R
9. EDGE	R

T 160 APATITES

TABLE 5.

	1	2	3	4	5	6	7
CaO	54.35	53.21	54.02	54.19	54.19	52.84	53.87
Na ₂ O	0.00	1.45	0.00	1.11	0.82	0.75	0.80
SrO	0.00	0.72	0.00	0.48	0.00	1.04	0.59
Y ₂ O ₃	1.13	0.00	1.08	0.00	0.00	0.00	0.90
P ₂ O ₅	40.31	38.71	41.13	39.68	40.64	40.75	41.42
Total	95.79	94.08	96.23	95.46	95.65	95.38	97.58

Number of ions on the basis of 10(Ca+Na+Sr+Y)

Ca	9.897	9.465	9.902	9.599	9.734	9.649	9.605
Na	0.000	0.466	0.000	0.355	0.266	0.249	0.258
Sr	0.000	0.069	0.000	0.046	0.000	0.103	0.057
Y	0.103	0.000	0.098	0.000	0.000	0.000	0.080
P	5.801	5.440	5.956	5.554	5.767	5.878	5.837
x/6-x	0.03	0.10	0.01	0.08	0.04	0.02	0.03

- | | |
|-----------------------|---|
| 1. AP2 C | C |
| 2. AP2 E | R |
| 3. AP3 C LARGE TURBID | C |
| 4. AP3 E | R |
| 5. AP4 C | C |
| 6. AP5 C | C |
| 7. AP5 E | R |

T-142 REE MINERALS.

TABLE 6.

	1	2	3	4	5
La ₂ O ₃	14.387	15.238	14.481	10.532	19.445
Ce ₂ O ₃	24.313	25.708	24.235	19.249	28.885
Pr ₂ O ₃	1.28	2.242	1.569	0.995	1.828
Nd ₂ O ₃	5.73	6.138	6.275	4.627	5.68
ThO ₂	0.79	0.68	1.08	0.77	1.26
CaO	16.05	17.47	17.53	11.75	6.14
SrO	0.55	0.97	1.07	0.55	0.75
Na ₂ O	0.00	0.60	0.00	0.47	0.54
Total	63.10	69.04	66.24	48.95	64.53

Number of ions on the basis of 7.5 Oxygens

	7.5	7.5	7.5	7.5	7.5
La	0.927	0.893	0.882	0.880	1.388
Ce	1.555	1.496	1.466	1.596	2.046
Nd	0.081	0.130	0.094	0.082	0.129
Pr	0.358	0.348	0.370	0.374	0.393
Th	0.031	0.024	0.041	0.040	0.055
Ca	3.002	2.972	3.100	2.849	1.273
Sr	0.056	0.089	0.102	0.073	0.085
Na	0.000	0.184	0.000	0.208	0.203
Total	6.010	6.136	6.055	6.100	5.571

1. SYNCHISITE.

2. "

3. "

4. "

5. ?SYNCHISITE-BASTNEASITE INTERGROWTH.

T-159 SECONDARY REE MINERALS

TABLE 7.

	1	2	3	4	5	6
La2O3	23.25	24.17	28.18	0.37	5.72	9.82
Ce2O3	19.58	19.59	9.62	56.09	43.14	33.16
Pr2O3	3.27	3.51	4.54	0.00	0.40	0.76
Nd2O3	10.03	9.97	13.47	1.42	2.01	4.40
ThO2	0.52	0.94	0.87	0.90	1.40	1.78
CaO	3.96	4.25	3.71	3.30	2.95	2.74
SrO	0.50	0.41	0.39	0.00	0.00	0.39
MgO	0.00	0.00	0.00	0.00	0.00	0.00
Al2O3	0.00	0.00	0.00	0.00	0.00	0.00
P2O5	24.76	26.19	29.59	6.41	11.37	13.96
Total	85.87	89.02	90.37	68.47	66.99	67.01

Number of ions on the basis of 4 Oxygens

	4	4	4	4	4	4
La	0.390	0.388	0.425	0.011	0.151	0.242
Ce	0.326	0.312	0.144	1.668	1.128	0.811
Nd	0.054	0.056	0.068	0.000	0.010	0.018
Pr	0.163	0.155	0.197	0.041	0.051	0.105
Th	0.005	0.009	0.008	0.017	0.023	0.027
Ca	0.193	0.198	0.163	0.287	0.226	0.196
Sr	0.013	0.010	0.009	0.000	0.000	0.015
Mg	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.000	0.000	0.000	0.000	0.000	0.000
P	0.953	0.964	1.025	0.440	0.687	0.789
Total	2.098	2.091	2.039	2.464	2.277	2.203

1. RHABDOPHANE-(LA)

2. "

3. "

4. ? RHABDOPHANE-(LA), CERIUM MINERAL MIXTURE

5. "

6. "

TABLE 8.

T-153 & T-155 CARBONATES.

	1	2	3	4	5	6	7	8	9
CaO	55.31	37.82	35.15	58.11	20.35	32.32	36.84	27.08	37.25
MgO	1.32	6.07	5.47	0.32	5.02	0.80	1.05	1.43	1.18
MnO	0.56	3.73	4.59	0.80	0.55	5.99	4.91	7.80	5.68
FeO	0.22	10.66	15.48	0.24	36.71	21.36	13.97	23.07	14.61
SrO	0.20	0.24	0.00	0.00	0.00	0.30	0.34	0.00	0.26
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.09	0.54
Total	57.41	58.28	60.69	59.47	62.63	60.47	56.77	59.38	58.72

Number of ions on basis of 6 oxygens

Ca	1.911	1.312	1.202	1.957	0.721	1.175	1.383	1.010	1.352
Mg	0.064	0.293	0.260	0.015	0.248	0.040	0.055	0.074	0.060
Mn	0.015	0.102	0.124	0.021	0.015	0.172	0.146	0.230	0.163
Fe	0.006	0.289	0.413	0.006	1.016	0.606	0.409	0.671	0.414
Sr	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Calcite	95.57	65.59	60.12	97.87	36.07	58.76	69.16	50.48	67.58
Magnesite	3.18	14.64	13.01	0.75	12.38	2.02	2.74	3.71	2.98
Rhodochrosite	0.76	5.11	6.21	1.07	0.77	8.61	7.29	11.50	8.15
Siderite	0.30	14.43	20.66	0.32	50.78	30.31	20.47	33.57	20.69
Strontianite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Witherite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00

1. T-153 CLEAR CARBONATE
2. " DARK CARBONATE
3. " "
4. " VEIN CARBONATE
5. " ? CARBONATE
6. T-155 DARK CARBONATE
7. "
8. "
9. "

T-155 APATITES.

TABLE 9.

	1	2	3	4	5	6	7
CaO	53.87	53.71	52.56	51.67	53.48	53.96	52.54
Na ₂ O	0.48	0.00	0.54	0.63	0.00	0.58	0.58
SrO	1.48	1.05	1.43	1.25	0.84	1.08	0.64
Y ₂ O ₃	0.00	1.41	0.91	0.00	1.09	0.00	1.67
P ₂ O ₅	41.67	41.34	41.04	40.88	42.01	41.75	41.34
Total	97.50	97.50	96.48	94.43	97.41	97.36	96.77

Number of ions on the basis of 10 (Ca+Na+Sr+Y)

Ca	9.700	9.770	9.599	9.659	9.818	9.708	9.592
Na	0.156	0.000	0.177	0.214	0.000	0.188	0.193
Sr	0.145	0.103	0.141	0.126	0.083	0.105	0.064
Y	0.000	0.127	0.083	0.000	0.099	0.000	0.151
P	5.929	5.941	5.923	6.039	6.094	5.935	5.964
x/6-x	0.01	0.01	0.01	-0.01	-0.02	0.01	0.01

1. CLEAR GRAINS

2. "

3. "

4. "

5. "

6. "

7. "

T 153 REE MINERALS

TABLE 10.

	1	2	3	4	5	6	7
La2O3	19.98	21.90	21.69	21.37	19.53	17.19	16.06
Ce2O3	31.17	33.15	32.29	30.29	30.06	27.76	25.57
Pr2O3	2.57	2.69	1.81	1.57	2.28	2.25	2.32
Nd2O3	7.98	7.09	6.70	6.08	6.82	6.91	7.03
ThO2	0.00	0.83	0.75	0.00	0.77	0.84	0.63
CaO	1.09	1.56	3.12	5.82	8.63	11.48	15.28
SrO	0.96	0.77	1.17	0.94	0.86	0.84	0.85
Na2O	0.00	0.67	0.80	1.09	0.84	0.62	0.55
Total	63.75	68.66	68.33	67.16	69.79	67.89	68.29

Number of ions on the basis of 9 Oxygens

	9	9	9	9	9	9	9
La	1.865	1.878	1.826	1.756	1.504	1.314	1.168
Ce	2.888	2.821	2.698	2.471	2.298	2.106	1.847
Nd	0.237	0.228	0.151	0.127	0.173	0.170	0.167
Pr	0.721	0.589	0.546	0.484	0.509	0.511	0.495
Th	0.000	0.044	0.039	0.000	0.037	0.040	0.028
Ca	0.297	0.388	0.763	1.389	1.930	2.547	3.228
Sr	0.140	0.104	0.155	0.121	0.104	0.101	0.097
Na	0.000	0.302	0.354	0.471	0.340	0.249	0.210
REE Total	5.712	5.516	5.221	4.839	4.484	4.101	3.677
Total	6.148	6.353	6.531	6.820	6.895	7.038	7.241

TABLE 11.

T 153 SECONDARY REE MINERALS

	1	2	3
La2O3	6.62	6.51	4.96
Ce2O3	9.02	9.71	7.09
Pr2O3	0.84	0.56	0.40
Nd2O3	2.16	2.33	0.85
ThO2	0.00	0.00	0.00
CaO	0.80	0.31	13.27
SrO	5.48	4.49	5.93
MgO	0.00	0.39	0.44
Al2O3	28.34	26.88	22.12
P2O5	25.10	25.37	20.39
Total	78.36	76.55	75.44

Number of ions on the basis of 11 Oxygens

	11	11	11
La	0.229	0.229	0.187
Ce	0.309	0.340	0.265
Nd	0.028	0.019	0.015
Pr	0.072	0.079	0.031
Th	0.000	0.000	0.000
Ca	0.080	0.032	1.450
Sr	0.297	0.249	0.351
Mg	0.000	0.054	0.065
Al	3.129	3.027	2.661
P	1.989	2.051	1.760
Total	6.135	6.080	6.783

1. FLORENCITE
2. "
3. ?FLORENCITE+CALCITE

TABLE 12.

DUPLICATE ANALYSES OF STANDARD

	1	2	3	4	5	6	7	8	9	10	11	12
CaO	55.26	55.07	55.92	55.22	55.22	55.85	56.12	55.34	55.41	54.77	55.42	0.40
Na ₂ O	0.00	0.00	0.00	0.00	0.46	0.00	0.48	0.49	0.00	0.00	0.00	0.00
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P ₂ O ₅	42.14	41.72	42.24	41.96	42.20	42.15	42.31	42.41	41.85	41.59	42.05	0.25
Total	97.39	96.79	98.16	97.18	97.88	98.00	98.91	98.24	97.26	96.35	97.47	0.65

Number of ions on the basis of 10 (Ca+Na+Sr+Y)

Ca	10.000	10.000	10.000	10.000	9.852	10.000	9.847	9.842	10.000	10.000	10.000	0.070
Na	0.000	0.000	0.000	0.000	0.148	0.000	0.153	0.158	0.000	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P	6.025	5.986	5.968	6.003	5.949	5.963	5.866	5.959	5.967	6.000	5.996	0.041
x/6-x	-0.00	0.00	0.01	-0.00	0.01	0.01	0.02	0.01	0.01	0.00	0.00	0.00

1-10 DUPLICATE ANALYSES OF APATITE STANDARD

11 MEAN

12 STANDARD DEVIATION

ASSUMED COMPOSITION CaO 55.35, P₂O₅ 42.02