Detection of trace elements in apatite crystals from Panasqueira, Portugal, by non-destructive optical methods, especially polarospectrography

A. A. F. Lagerwey

Lagerwey, A. A. F. Detection of trace elements in apatite crystals from Panasqueira, Portugal, by non-destructive optical methods, especially polarospectrography. — Scripta Geol., 42: 1-52, 13 figs., 4 pls., Leiden, September 1977.

A selection of well developed apatite crystals of different habit and colour, originating from the tungsten-tin deposits of Panasqueira in Portugal, were analyzed by means of non-destructive optical methods. Phenomena of pleochroism, absorption and luminescence line-spectra, broadband-spectra and phosphorescence were studied.

On the basis of extensive and systematic data, obtained from more than seven-hundred polarized spectrophotograms, registered of about seventy apatites from different types of deposit, and of a whole range of fluorapatites, doped with lanthanides and transition elements, it was possible to define the particular type of crystalfield and the nature and quantity of a number of trace elements, present in the fluorapatite from Panasqueira.

Strong pleochroism is observed in green crystals from Panasqueira. The blue colourcomponent, intensely polarized parallel with the main axis and concentrated in topologically significant areas at the intersection of (0001) and (11$\bar{2}$0), is explained by the presence of O^{1-} electron defects in the halogen-ion chains. The yellow-green coloration, which is not perceptibly polarized, and is distributed evenly throughout the volume of the crystals, is caused by MnO_4^{1-} ions replacing $(PO_4)^{3-}$ anionic groups.

Absorption line-spectra reveal the presence of 110 ppm of Nd^{3+} in Ca^{2+} sites in a representative crystal, and make it possible to assign the Panasqueira apatite to a group of typical apatites, characterized by their crystalfield-configuration; the apatites from the tin-tungsten deposits near Ehrenfriedersdorf in Saxony also belong to this group.

Luminescence line-spectra do manifest the same typical fieldeffects in the Pr and Nd line groups. The presence was established of the following ions: Pr^{3+} (11 ppm), Nd^{3+} (110 ppm), Sm^{3+} (55 ppm), Eu^{3+} (10 ppm), and Dy^{3+} (25 ppm). Traces of Tb^{3+} could also be detected, but lanthanides with an atomic number higher than 66 could not be found.

By comparison of the distributions of the lanthanide elements in the apatites from Panasqueira and in an average apatite, statistically defined, it is demonstrated that the lanthanides of higher atomic number are significantly enriched.

Broadband-luminescence spectra demonstrated the presence of Mn^{2+} ions in a Ca^{2+} site (0.2% by weight), with an intensity maximum near 580 nm. Eu^{2+} (< 10 ppm) is concentrated in the basal layers of a special type of crystal; the blue luminescence has a maximum at 450-430 nm.

Phosphorescence-effects are thought to be caused by Mn^{2+} in Ca^{2+} sites of different coördination. There is a rather narrow green emissionband with a maximum near 550 nm.

Finally, the existence of a correlation between specific assemblies of variables, such as: external distinctive marks, crystalfield-configuration and quantitative distribution of lanthanides, which are characteristic for certain constitutional types of apatite, is outlined.

A. A. F. Lagerwey, Laboratory for Crystaloptics and Physics Research, Grote Stegel 13, Eijgelshoven (L), The Netherlands.

Introduction

The magnificent crystallized mineral samples from Panasqueira in Portugal, now exhibited in many musea, are rapidly becoming famous. These samples do not only show us the complete suite of ores and accessory minerals in their order of deposition, but also the varied and often perfect development of individual crystals.

The crystals of apatite, seated on large and splendid crystals of quartz, wolframite or arsenopyrite, in particular, attract the vivid attention of the interested mineralogist or physicist. Almost every researcher is puzzled by the range of habits, the zoning and colouring of the apatite crystals from Panasqueira. The problem for these analytical minds, realizing the exclusivity of the much coveted large crystals, is, of course, how to find a way to get as much information about the crystal's interior and build without destroying them.

In the present article, the author will try to demonstrate the possibilities of nondestructive optical and polarospectrographical methods and the apparatus, developed especially for such a purpose. The apparatus and the method are relatively simple: no expensive or dangerous sources of radiation, no cryostats, no complicated electro-optical recording systems, no computers are required. Still, a wealth of well documented, objective information, very difficult to obtain in any other way, can be produced. Of necessity, because of the intricacies of the material — apatite — and of the fundamentals of the optical methods involved, this study cannot be much more than a sketch. It is the intention of the author, that this sketch should bring forward results so tempting, as to incite other research workers to follow the line.

In the course of this study, we will show, describe and analyse the topography of colours and the phenomena of pleochroism observed in some large crystals from Panasqueira, and compare their nature with those observed in apatite crystals from other deposits. Next, being armed with an extremely sensitive method allowing the detection of trace elements, forming centres of optically active ions in the crystal lattice, we will analyse the absorption line-spectra, the luminescence line-spectra, and the broadband spectra of the crystals mentioned. Detailed structures of groups of spectral lines of single trace elements are revealed in the spectrophotograms shown in the text. It will be demonstrated that line-patterns, characteristic for special types of apatite as regards the crystal-field in the vicinity of the bivalent calcium sites, can be distinguished.

With the aid of a range of synthesized fluorapatites, doped with known concentrations of lanthanide elements, we will prove — by means of comparison — which of these elements are present in the apatites from Panasqueira. In some cases, combined analysis of absorption and luminescence will make it feasible to estimate concentrations.

The analysis of the broadband spectra will tell us about the presence of ions of some transition-metals, and about the presence of bivalent lanthanide ions. It is also possible to gain an insight into processes of energy transfer between active ions. Attempts are described to analyse phosphorescence, exhibited by some crystals after excitation with photons of higher energy.

In the final section of the paper, the results of analyses are evaluated and synthesized into a conclusion. This conclusion comprises significant data about structures, causing pleochroism, and about the quantitative distribution of trace elements, causing the spectacular luminescence and absorption phenomena. The resulting quantitative distribution of lanthanides in the Panasqueira apatite crystals is compared with a proposed normal distribution in apatite in general, and with the geochemical abundance of these elements. The distribution pattern is then compared with the distribution patterns of oher types of apatite, characterized by the fine-structure of their neodymium-spectrum.

References to the work of other authors are frequently made in the text, and reactions and suggestions are invited.

Acknowledgements

The author expresses his great appreciation for the fine work, done by the staff of the Rijksmuseum van Geologie en Mineralogie (the Netherlands National Museum of Geology and Mineralogy) under the direction of Dr P. C. Zwaan, to whom he is particularly indebted for his advice and active co-operation. He also wishes to thank Mr H. Schwabe of Herzogenrath for his excellent work in the processing of the voluminous photographic material.

Characteristics of the Panasqueira mineral deposit

THE PANASQUEIRA PARAGENESIS; APATITE

The famous tungsten mines, named after the village of Panasqueira, are situated in central west Portugal, in the province of Beira Baixa. The mines are actually located in a depression, named Cova da Beira. This depression is located between the mountainranges of Guardunha and of São Pedro de Açor.

The geology and mineralization of the Panasqueira group of mines have been extensively and expertly described. It would not serve any practical purpose to fill this paper with a repetition of established facts. For this reason, we will only mention the main characteristics of the deposit, and discuss the formation of the apatites. For the rest, we would like to refer to the publication of Cardoso d'Orey (1967), which contains very precise data and many references. The practical mineralogist will find a good review of the situation in the article of Gaines and Thadeu (1971).

The mineral deposits of the Panasqueira group all originate from a large granite intrusion. Vapours and solutions from this magmatic source intruded the overlying sedimentary rocks of Infracambrian age. In this formation, the minerals were formed by reaction and deposition: the ore bodies thus formed are of a lenticular shape; they are lying nearly horizontal. The country-rock consists of slates and sandstones. The mineralization is of the quartz-tin-tungsten type, and can be classified as pneumatolytic, modified by later hydrothermal activity. The character of the mineralization at Panasqueira is very similar to those of the Erzgebirge (Saxony, GDR) and of Cornwall and Devonshire in England.

The mineral deposits of Panasqueira are not uniform in character, and it is necessary to make a distinction between two types of mineralization, which clearly are to be ascribed to two distinct sources of emanation. These two complexes are geographically separated and are named after their respective sites:

— the Panasqueira - Barroca Grande complex, and
— the complex of the Vale da Ermida.

In both deposits, the sequence of mineralization is different. The Panasqueira deposit does not show a very distinct zoning, which could arise from a well differentiated sequence of deposition. It is abundant in wolframite. Rather thick selvages of a greyish green muscovite were deposited in an early stage; most of the apatite crystals have developed in these selvages. The Vale da Ermida deposits show a very distinct zoning. The deposits are abundant in cassiterite rather than in wolframite, they are bearing more noble metal, and the selvages of muscovite are much thinner.

The apatite crystals, which form the subject of this study, all originate from the Panasqueira - Barroca Grande complex. The crystals must have been formed in the initial stages of higher temperatures, somewhat later than the stage during which the deposition of the primary muscovite took place. The period of formation of the apatite overlaps the period of formation of the wolframite. Often, therefore, the apatite crystals are based on crystals of wolframite, or on aggregates of quartz crystals and wolframite crystals. The larger apatite crystals are clearly zoned, thus telling of several periods of growth with distinct intervals of stagnancy or discontinuities in composition of the mineral-bearing solutions. The apatite crystals are often corroded by muscovite of a later deposition and by quartz. Crystals of arsenopyrite seem to have been deposited in a later stage; they are often found in close contact with the apatite crystals. Secondary pyrites are sometimes seen to be deposited in beautiful accumulations on the top faces of the larger crystals of apatite. Minor associates of apatite are siderite and calcite.

Fluor must have been an important element in the ore bearing solutions, if one is to judge from the quantities of apatite deposited. Fluorite, however, is found to occur only in the southernmost veins of the Vale da Ermida complex. This mineral is certainly much less abundant in the Panasqueira deposits, than in the related mineralizations of the Erzgebirge and Cornwall.

DESCRIPTION OF APATITE CRYSTALS; A COMPARISON WITH APATITES FROM EHRENFRIEDERSDORF

Although the crystals of apatite from Panasqueira are displaying a great variety of colours and hues, and also of crystal habit, the great majority are of a typical green or greyish green colour; the usual habit is short prismatic with a perfectly developed basal pinakoid (0001). The first order prism $(10\bar{1}0)$ is predominant over the second order prism $(11\bar{2}0)$. The two prisms often alternate: this results in spectacularly striated faces such as are frequently observed in tourmalines.

The prominent zoning of the crystals shows itself in layers of different colourshade and colour density. Very characteristic of crystals of this generation is the appearance of a concentration of an intensely blue-green pleochroic complex near the intersection of the basal plane (0001) and the prism $(11\bar{2}0)$. Next, there is a generation of apatites of a beautiful rose-purple or lilac colour, exhibiting essentially the same crystal habit. This colour is sometimes shared with green in parti-coloured crystals: here, the lilac colour is found most frequently in the outer prismatical layers.

As a rarity, tabular crystals are found which are heavily corroded and overgrown with a later generation of muscovite crystals in spectacular rosettes. The interior of these crystals is practically colourless, but the outer layers are intensely coloured blue.

The characteristics, given here, do apply in a marked degree to the crystals of apatite, occurring in the tin-tungsten deposits of the Erzgebirge, and it seems worthwhile to define similarities and differences, which might be related to particularities of the respective parageneses.

Plate 1, figure 1 shows two twin aggregate crystals: the smaller aggregate (S. 388 from the author's collection) was taken recently from the workings of the tin-mine 'VEB Zinnerz und Spatgruben', located on the Sauberg in Ehrenfriedersdorf, while the larger aggregate (S. 406) originates from Panasqueira-Barroca Grande (in future we will only mention 'Panasqueira' to indicate this mining complex). One is struck by the almost perfect similitude of habit and colour of the main body of the crystals, and particularly by the identical nature and development of the bluegreen zones on the edges.

Both in Panasqueira and in Ehrenfriedersdorf, these light green crystals are frequently accompanied by long, perfectly developed and highly lustrous crystals of arsenopyrite. In both deposits, the element arsenic is present in great quantities, and it should be noted that arsenic is sometimes incorporated in the apatite lattice, presumably in the anionic group AsO_4^{3-} replacing a PO_4^{3-} group (Haberlandt, 1938, p. 148, 149. Arsenic in yellow apatite from Jumilla, Murcia, Spain). Well developed coatings of apatite with rosettes of muscovite are likewise observed in both deposits.

Another very striking similarity between the two deposits consists in the occurrence of rose-purple or lilac coloured crystals of apatite. Lilac crystals from Ehrenfriedersdorf were formerly only known to originate from an ancient working, situated near the Greifensteine, between Ehrenfriedersdorf and Geyer, but they are now also found in the active part of the tin mine. These lilac crystals show the same characteristics and colour as similar crystals from Panasqueira. These evenly coloured crystals are rare, however. The lilac colour is more frequently observed in the outer prismatical zones of the green crystals from Panasqueira. In the section on pleochroism we will see that these lilac zones are not pleochroic, and that the colouring in the Panasqueira apatites is of the same nature as the lilac colouring of the apatites from Ehrenfriedersdorf.

There are, however, also differences: the apatites from the Sauberg working are much less corroded and altered by secondary processes than those from Panasqueira. In the latter deposit, the development of the muscovite selvages is much more important than at the Sauberg, although samples can be produced from this mine which are almost identical in appearance. We will also prove that the Portugese apatites have a much higher content of elements of the lanthanide group (formerly called 'Rare Earths'). These differences can be related to relatively minor differences in paragenese: in the Sauberg deposit, cassiterite is much more abundant than wolframite. The apatite crystals are less directly associated with quartz and wolframite. Fluorites are much more abundant and varied in zoning and colour. Finally, the Sauberg deposit carries more noble metals, notably silver, than either the Panasqueira deposit or the one of Vale da Ermida.

The green apatite crystals from both deposits show a good fluorescence of a mustard-yellow colour under long- and shortwave ultraviolet radiation. This fluorescence is caused by bivalent ions of manganese.

SELECTION OF CRYSTALS FOR OPTICAL ANALYSIS

Single crystals are the most appropriate objects for the non-destructive optical methods of analysis, devised and developed by the author. As this study does not permit extensive explanations and considerations of a technical nature, we should like to refer here to the authors publications, mentioned in the list of references.

The size of the crystals should be sufficient to permit accurate orientation for the purpose of research of polarization phenomena. For the polarospectrographical analysis, the cross section of the crystals need not be more than one or two millimeters. Complex samples are preferable, because they may show the nature and composition of the environment, in which the crystals examined have developed. This environment, naturally, has a decisive influence on the properties of the crystals. For optical investigations, the crystals, seated on a sample, should be in an accessible position, preferably on the periphery.

On the other hand, when studying effects of colour, the composition of different zones, the topographical distribution of pleochroic complexes, the general development of crystal faces, the phenomena of exsolution or redeposition, diffusion, etc., it will clearly be an advantage to use larger individual crystals.

The Rijksmuseum van Geologie en Mineralogie and the private collection of the author contain a number of excellent complex samples and single crystals. This made it possible to effect a selection of objects suitable for optical investigation. Here one should, of course, take good care to choose crystals, which are representative for certain types or generations of apatite crystals, characteristic of the deposit. The selection of freak crystals has to be avoided.

An opposing consideration is that individual crystals of a larger size and prominent development and colouring, or crystals showing strong pleochroism, luminescence or phosphorescence for example, allow a more accurate analysis to be made.

The results of an investigation are generally more accurate and applicable, if the number of objects investigated is large. Here again, a limit is imposed by restrictions of time and means available. As the author already explained in the introduction, this study is only intended to be a demonstration of the possibilities, created by the recently developed non-destructive optical method. It must not be regarded as a detailed and rounded-off chapter of research.

Armed with the consciousness of these considerations, a number of complex samples with apatite crystals, and some larger individual crystals were selected: they are described in detail in the following section:

S. 248 — Dark green crystal of short prismatic development. It measures 50 mm across, and its height is 26 mm. This crystal displays a uniform and intense pleochroism, which will be analysed in the appropriate chapter. The body-colour of the crystal is rather difficult to define. Colours are best judged in diffuse daylight. In order to give a reasonable definition of colours, the colour chart of the Royal Horticultural Society (1975) is used throughout this study. This chart is accompanied by a table of cross-references, in which the coördinates of the colour-point in the C.I.E. (Commission Internationale de l'Eclarage) diagram are also given.

In the author's eyes, the body-colour of the crystal is best reproduced by sample (R.H.S.) 147 A, a sort of dark peridot green. The coördinates are $x = 0.330$, $y = 0.400$, and $Y = 8.1$. When observing the colour of the light, transmitted in the direction of the c-axis, a chartreuse green, 154 B, with coördinates $x = 0.401$, $y = 0.477$, and $Y = 73.1$ appears.

The following development of crystal faces is observed:

a $(10\bar{1}0)$. First order prism well developed, slightly striated.
b $(11\bar{2}0)$. Second order prism, narrower and more intensely striated.
c (0001). Basal pinakoid, largely developed; very smooth.
x $(10\bar{1}1)$. First order pyramid, very narrow, mirror like.
r $(10\bar{1}2)$. First order pyramid, idem.
s $(11\bar{2}1)$. Second order pyramid, rather well developed; strongly etched.

These last pyramidal faces have a very curious appearance indeed. From these faces, flattened capillaries of prismatical cross section deeply penetrate into the crystal, strictly parallel to the c-axis. They give rise to the impression of a fibrous structure. Photographs of this crystal in polarized light are shown on Plate 2, fig. 1.

The crystal luminesces rather strongly in long- and short-wave ultraviolet light, revealing a pronounced prismatical zoning. The colour of the emitted light is a saturated mustard-yellow.

S. 362 — A very transparent crystal with short prism faces and a spectacular pyramidal development. It measures 60 mm across the base, it is 50 mm high and 36 mm deep. The two planes of attachment are very smooth, being suggestive of wolframite as the original basis. It displays pronounced, but localized pleochroism; this will be analysed extensively in the next chapter. The body-colour of the crystal appears to the eye as a light pea-green colour, very similar to (R.H.S.) 148 D, coördinates: x= 0.340, y= 0.369, and Y= 43.3. Near the base, a slight blue-green pleochroic hue can be observed without the aid of a polarizer. This colour can be qualified as light capri-blue, 120 C, with coördinates x= 0.250, y= 0.296, and Y= 39.9.

In the centre, a darker green colour of cloudy appearance can be seen. Zoning is very slight; it is congruent with the exterior faces of the crystal. In the interior, a system of small cracks is visible, and the crystal has been cleaved, roughly following $(10\bar{1}0)$, by pressure. The cleavages have been partly regenerated. A second generation of muscovite crystals developed in a thin layer in a remaining open cavity.

The habit of the crystal is very remarkable, this being occasioned by the extraordinary development of the pyramidal face $(20\bar{2}1)$. The drawing, Figure 1, represents the crystal. The main faces are:

a $(10\bar{1}0)$. Main prism faces well developed, slightly striated parallel with the c-axis.
b $(11\bar{2}0)$. Secondary prism faces, much less developed, very slightly striated.
c (0001). Well developed, but not dominating. Heavily etched, showing congruent zoning. Under magnification, the projections show pyramidal faces.
x $(10\bar{1}1)$. Pyramidal faces are very narrow; surface mirror like.
r $(10\bar{1}2)$. The development is the same.
y $(20\bar{2}1)$. This first order pyramid is predominant; the very large face is perfectly plane and smooth, showing only the slightest etching.
s $(11\bar{2}1)$. This second order pyramid is beautifully developed in narrow, longitudinally developed, mirror like faces.

The capillaries, noted in S. 248, are absent.

The luminescence, excited by short-wave ultraviolet radiation is rather intense, showing yellow and reddish hues. When examined with the aid of a pocket spectroscope, the absorption lines of trivalent neodymium were found to show up rather distinctly. For all these reasons, the crystal appeared to be very suitable for a study of pleochroism as well as for spectrographical analysis.

S. 363 — A complex sample. It consists of an aggregate of tabular apatite crystals of a greyish-blue to a steel-blue colour. The apatite crystals are covered with a layer of muscovite crystals of about 1.5 mm thickness. The muscovite was obviously deposited in a later stage. This muscovite severely corroded the apatite crystals. On top of the muscovite layer, some minor siderite was deposited. Admixed with the siderite, a separate, later generation of apatite-like crystals are noted. They are stained by limonite, but otherwise appear to be light coloured and slightly pearly in appearance. Possibly, they consist of a wilkeite-like apatite, similar to the crystals, mentioned by Gaines (Gaines & Thadeu, 1971, p. 77). The single crystals of apatite reach a diameter of 30 mm, and a thickness of 9 to 10 mm.

The body-colour of the crystals is a greyish green, which can be qualified as willow green (R.H.S.) 196 B with coördinates x= 0.329, y= 0.344, and Y= 57.1. In stark contrast with this rather dull colour, the top- and contactfaces of the crystals are tinted a very bright blue, which is similar to oriental blue 110 B, coördinates x= 0.188, y= 0.213, and Y= 23.1. In artificial incandescent light the crystals are looking almost grey; this shows that the blue colour is caused by a very strong absorption of red rays. The photograph, reproduced on Plate 1, figure 2, clearly shows that the blue colour complex is concentrated in a layer of about 1 mm thickness, adjacent to the curiously striated rear face of contact. The crystals appear to be halved by this face. Pleochroism is very pronounced, the colours being blue and colourless.

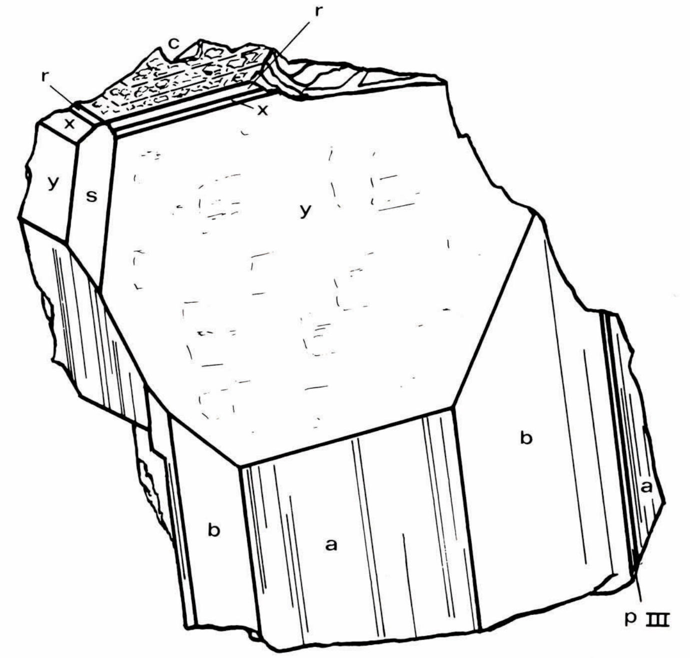

Fig. 1. Habit of a large apatite crystal from the Panasqueira Mine (sample S. 362). Height 50 mm. Pleochroic colours // c-axis: blue-green, ⊥ c-axis: pale yellow-green, concentrically zoned. Crystal faces a=$(10\bar{1}0)$, b=$(11\bar{2}0)$, c=(0001), x=$(10\bar{1}1)$, r=$(10\bar{1}2)$, y=$(20\bar{2}1)$, s=$(11\bar{2}1)$; p III= prism of the third order.

An interesting feature is the presence of hexagonal pits, which are probably the consequence of local redissolution. These pits are located in the basis (0001), and also in amply developed pyramidal faces. Beautiful rosettes of muscovite crystals have been formed in the pits. Particularities of the crystal-habit are shown in Figure 2; etched patterns and a nest of muscovite crystals are indicated.

The larger crystals of the aggregate show an interesting development of faces. Figure 3 represents an accurate perspective sketch of one of the larger crystals. The main faces noted are:

a	$(10\bar{1}0)$.	Main prism well developed, heavily striated.
b	$(11\bar{2}0)$.	Second order prism faces slightly narrower; they show tiny etchings, but are otherwise perfectly smooth.
c	(0001).	Basis well developed, with beautiful hexagonal etched figures and some hexagonal pitting.
r	$(10\bar{1}2)$.	Pyramidal face, amply developed, brilliant surface.
α	$(10\bar{1}3)$.	Idem, relatively narrow, matt, etched surface.
β	$(10\bar{1}4)$.	Pyramidal face, narrow, more heavily etched.
s	$(11\bar{2}1)$.	Small, brilliant faces.

The crystals are homogeneous and clear; in some of them shell-shaped flat inclusions were noted.

The luminescence under shortwave ultraviolet radiation is homogeneous, and of a mustard-yellow colour. Phosphorescence after irradiation is much weaker and more short lived than with S. 362. The absorption lines of trivalent neodymium can be observed in the blue crystals, but they are less intense than the lines observed in S. 362.

This complex sample was selected by reason of its unusual crystal habit — as compared to the other generations of apatite crystals from Panasqueira — and the intense blue coloration.

RGM 251 424 — Another aggregate sample. It is composed of an assembly of well developed and highly lustrous crystals of arsenopyrite, intergrown with dense masses of splendidly piled up hexagonal crystals of muscovite of a greenish tint. Embedded in this cluster one finds a group of small tabular apatite crystals of the

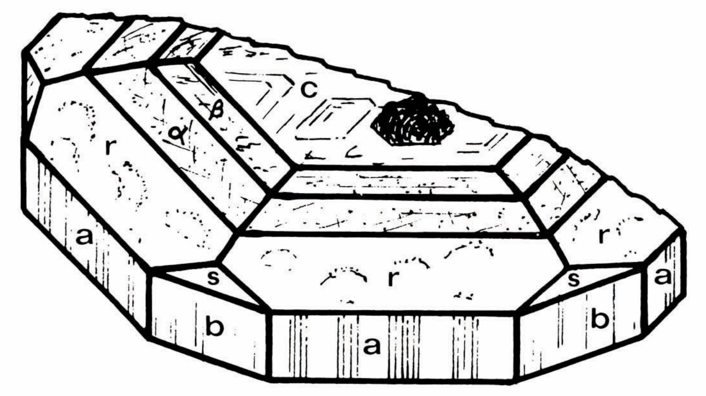

Fig. 2. Typical habit of some blue-gray lenticular apatite crystals from the Panasqueira Mine (sample S. 363), this specimen shows a nest of muscovite crystals in a solution cavity (on top). Rear face ribbed. Body colour greenish gray, bright blue on ends. Crystal faces a=$(10\bar{1}0)$, striated, b=$(11\bar{2}0)$, smooth, c=(0001) brilliant, r=$(10\bar{1}2)$ brilliant, well developed, α=$(10\bar{1}3)$ narrow, etched, β=$(10\bar{1}4)$ idem, s=$(11\bar{2}1)$ small, brilliant.

usual greyish-green colour, measuring up to 6 mm across and reaching a thickness of 3 mm. This complex sample is remarkably like samples of the same nature which originate from the Sauberg tinmine near Ehrenfriedersdorf. This sample was selected because it seemed to be representative of the average type of apatite, occurring in the Panasqueira deposit.

Analysis of pleochroism in apatite crystals

In the preceding description of samples we have seen, that striking effects of pleochroism — they are even visible to the unaided eye — are observed in many samples of apatite from Panasqueira. The interesting topographical distribution of colour-effects in zones of growth, or in other specific areas linked with certain crystallographic elements of the crystals, suggest important changes in the chemical nature of the environment during the period of development, as well as physico-chemical actions, such as ion-diffusion processes during more latent phases. Therefore, it is of great interest from a geochemical point of view, to study these phenomena in more detail, and to attempt to make an analysis.

DESCRIPTION OF METHODS AND OBSERVATIONS

The methods of analysis are, of course, determined by the variables dominating the complex of phenomena. Variables of an indicative nature are:

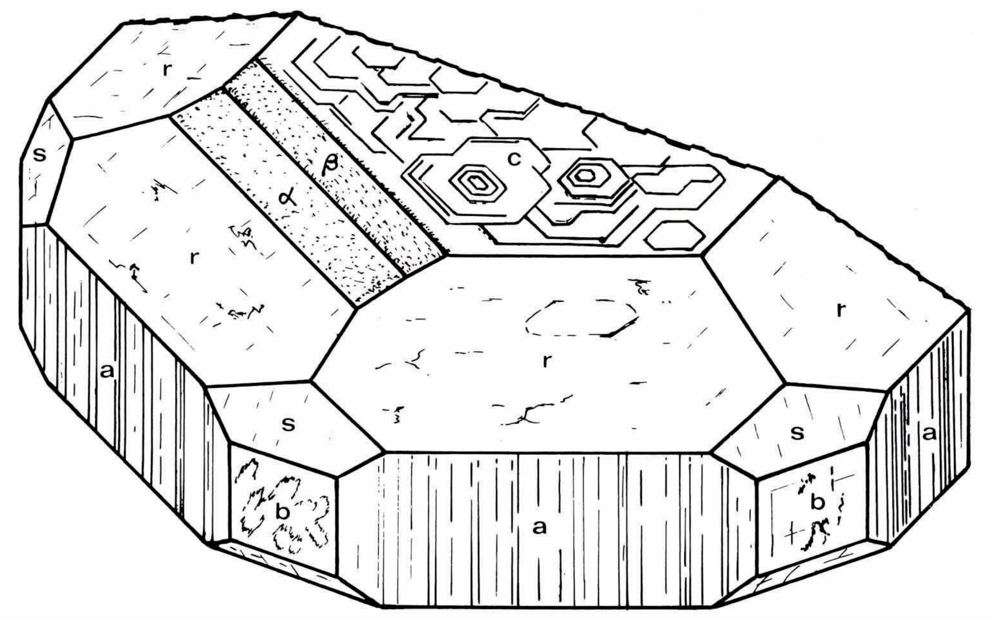

Fig. 3. Habit of a short prismatic apatite crystal from the Panasqueira Mine (sample S. 363), showing the full development of faces. Striated face of contact. Body colours greyish blue, pleochroic colours // c-axis: blue, ⊥ c-axis: colourless; blue colour concentrated in zone of contact with rear face. Diameter 30 mm. Crystal faces a=$(10\bar{1}0)$, b=$(11\bar{2}0)$, c=(0001), r=$(10\bar{1}2)$, α=$(10\bar{1}3)$, β=$(10\bar{1}4)$, s=$(11\bar{2}1)$.

The spectral composition of colour complexes, coupled to significant crystallographic directions.
The topographical distribution of colour complexes, coupled to particularities of the crystal-lattice, indicative of the nature of physico-chemical processes.
Of course, there are other important variables, such as effects of temperature, but we will leave these out: when studying such effects, we would have to deviate from the adopted principle of non-destructivity.

For the evaluation of the effects of these variables, the author was limited to two instrumental methods:

A) Spectrophotometry of transmitted light in significant directions of the electrical vector $\vec{E}$ relative to the crystallographic axis.
B) Observation of colour complexes in convergent light with the aid of a polarizer of high optical quality and means of accurate angular orientation of polarizer and crystal. Here, the main variable is the topographical distribution.

As these means are well-known, and simple enough, we will refrain from further technical details. Explanations will be given, where necessary.

We have seen already that pronounced effects of pleochroism can be observed in the samples S. 248, 362 and 363. Except perhaps in S. 248, the pleochroic complexes are strictly non-isotropical in distribution. In the Panasqueira apatites, pleochroism is most marked in crystals of a dark-green body colour, or in crystals, showing colour zoning or localized colour complexes, The pink crystals, or the crystals, parti-coloured pink and green, do not show observable effects of pleochroism. These crystals are exactly similar in their behaviour to the lilac or violet crystals of Ehrenfriedersdorf. It must be remarked here that the colour is really either a red-purple or a violet-purple, and not really a pink or rose colour. Typical is R.H.S. 76 B: x = 0.313, y = 0.274 and Y = 54.6.

We will now proceed with accurate descriptions of the effects, observed in specific samples.

S. 248 — This dark-green crystal shows strong and uniform pleochroic effects. Plate 2, fig. 1 shows photographs of this crystal in polarized light. In Plate 2, figure 1a, the light is polarized parallel with the main crystallographic axis c (notation: $\vec{E}$ // c); it shows the intense and uniform blue-green colour, which is similar to R.H.S. 118 A, Indian blue, with coördinates x = 0.186, y = 0.246 and Y = 20.7. On close examination, this blue complex, which we will consider as an entity and label 'B', appears to be concentrated in a prismatic layer with a uniform development in the direction of the c-axis. In a radial direction, it forms a mantle with rather diffuse boundaries of about 3 mm thickness. This is the reason why the distribution of 'B' appeared to be a uniform one; in reality it is radially anisotropic. When rotating the polarizer, the blue colour 'peaks' very sharply when $\vec{E}$ is exactly parallel to the c-axis. This means that complex 'B' is strongly polarized. In Plate 2, figure 1b, the light is polarized perpendicular to the c-axis (notation: $\vec{E} \perp c$). The colour is most similar to R.H.S. 154 B, Chartreuse green, coördinates x = 0.401, y = 0.477 and Y = 73.1. It is not a very saturated colour. We will label this colour complex 'A'. The colour does not peak so sharply as 'B' does, it is practically unpolarized. Also, the colour is not appreciably zoned. It is therefore understood to be an independent complex, different from 'B'. In a later stage we will see that this observation is confirmed by spectrophotometrical data. For easier comparison of data, we summarize our findings in tabular form:

Complex 'B'. Polarization: $\bar{E}$ // c, strongly polarized.
Zoning : prismatical, congruent. Layer of 3 mm thickness.
Anisotropy : radial.
Colour : 118 A: Indian blue
x= 0.186, y= 0.246, Y= 20.7.
Complex 'A'. Polarization: practically unpolarized, observable with $\bar{E} \perp$ c.
Anisotropy : feeble, indeterminate.
Colour : 154 B: Chartreuse green
x= 0.401, y= 0.477, Y= 73.1.

S 362 — This large, well developed and clear crystal shows the same type of pleochroism as is observed in S. 248. Plate 3, figure 1 shows the crystal in light, polarized with $\bar{E}$ // c and $\bar{E} \perp$ c, respectively. In Plate 3, figure 1a we can observe the same blue colour of complex 'B', but modified by mixing with the yellow-green of complex 'A' to R.H.S. 121 A, a sort of Langite green, with coördinates x= 0.227, y= 0.280, and Y= 26.7. The distribution of this colour is much less homogeneous than in the case of S. 248. On detailed examination, the complex appears to be concentrated in different layers: the complex is primarily concentrated in a diffuse zone, penetrating the crystal from the two contactfaces (planes of growth). Next, it appears in a thin layer directly underlying the outer surface of the crystal, and lastly in the core of the crystal. As observed in S. 248, the intensity of the blue colour peaks very sharply, when the polarizing plane is exactly parallel to the c-axis. In the direction of $\bar{E} \perp$ c, a light-green colour is observed; it is similar to R.H.S. 154 C with coördinates x= 0.373, y= 0.435 and Y= 77.2. The colour is evenly distributed through the volume. Some opaque inclusions appear in clouds. If we are looking through the crystal in the direction of the main axis, a slightly more saturated greenish hue is perceived: R.H.S. 151 B, citron green, x= 0.419, y= 0.489 and Y= 52.2. The complex is not appreciably polarized. The observations are again summarized:

Complex 'B'. Polarization: $\bar{E}$ // c, highly polarized.
Zoning : congruent; concentration along planes of contact.
Anisotropy : unevenly distributed.
Colour : 121 A: Langite blue-green
x= 0.227, y= 0.280, Y= 26.7.
Complex 'A'. Polarization: The complex is not appreciably polarized.
Zoning : not observable.
Anisotropy : irregular.
Colour : 154 C: yellow-green
x= 0.373, y= 0.435, Y= 77.2.

S. 363 — The strong pleochroic phenomena have already been described in the paragraph dealing with the selection of the samples. If the crystals are observed through a polarizer with $\bar{E}$ // c, a very bright and rather saturated blue colour appears in the majority of them. This colour is qualified as R.H.S. 110 B, a sort of oriental blue with coördinates x=0.188, y= 0.213 and Y= 23.1. The blue colour peaks sharply, when the plane of the polarizer is oriented exactly parallel with the c-axis, showing the typical behaviour of the 'B' complex. Plate 1, figure 2 shows that this complex is concentrated in a layer of about 1 mm thickness close to the surface of contact. In a lesser degree it is observed in a very thin layer parallel to the end faces. With the polarizer oriented with $\bar{E} \perp$ c, the body of the crystal looks practically colourless or of a bleak grey colour. The yellow-green colour, which is characteristic for complex 'A', is not observed. Thus, in essence, the pleochroism observed in the blue crystals is of the same nature as the blue and yellow-green pleochroism which is observed in the other crystals; only the yellow-green 'basic' colour is lacking. For the same reason, the colour of the 'B' complex is a purer blue and not a blue-green tint. Summary of the observations:

Complex 'B'. Polarization: $\vec{E} \parallel c$, strongly polarized.
Zoning : Layer of 1 mm thickness along surface of contact, minor pyramidal or basal.
Anisotropy : perpendicular to contact-surface.
Colour : 110 B: Oriental blue
$x = 0.188$, $y = 0.213$, $Y = 23.1$.
Complex 'A'. Virtually absent.

RGM 251 424 — The apatite crystals pertaining to this sample are not well suited to observations on pleochroism.

The phenomena of pleochroism, observed in the crystals S. 248, S. 362 and in sample S. 363 show clearly that the pleochroic colourchanges are caused by two complexes of characteristic properties. The first complex, 'B', causes a characteristic blue or blue-green colour, which is caused by a stronger absorption in the red part of the spectrum. This absorption appears to have a maximum at about 720 nm and it is sharply polarized parallel to the main crystallographic axis. Figure 4 shows the transmission characteristics of polarized light in the wavelength-range between 400 nm and 750 nm; it is typical for the blue-green to yellow pleochroism, observed in crystal S. 362.

The second colourcomplex, 'A', gives rise to a more or less intense yellow-green colour. This hue is mainly conditioned by a stronger absorption of light in the blue and violet regions, as well as by a minor absorption with a maximum in the neighbourhood of 600 nm. The curve for the rays with $\vec{E} \perp c$ in Figure 4 clearly demonstrates the point. This complex does not show polarization in any marked degree. Therefore, it should be kept in mind that the curve for $\vec{E} \parallel c$ is really shaped by the resultant action of absorption of the complexes 'B' and 'A'.

To continue the summing up of the phenomenological observations, it must be remarked that the complexes do not only differ in optical nature, but also in a geometrical respect. While complex 'A' appears to be rather evenly distributed through the volume of the crystal, complex 'B' is markedly anisotropical. It tends to concentrate on faces of contact with other crystallized minerals like wolframite, or in zones adjacent to the exterior faces of the crystal at one time of development, with a preference for the pyramidal faces, or in areas concentrated around the intersection of faces $(11\bar{2}0)$ and (0001).

This geometrical singularity is linked clearly to discontinuities in growth versus time: the crystals show in their structure periods of growth, followed by relatively long periods of stagnancy due to changes in the chemical and physical environment. The complex 'B' was developed during these periods of altered surroundings. The description of the zoning, observed in crystal S. 362 demonstrates this point. Sometimes, in the Panasqueira deposit, we find crystals with an extraordinary development, showing the origin and character of the 'B' complex even more clearly. The drawing, reproduced on Plate 4, figure 1, depicts a flat prismatic crystal, showing colours and zoning. The singular nature of complex 'B' is most obvious, if one looks at the concentrations of blue-green colour.

Complex 'A', on the contrary, does not show such geometrical singularities. It is normally developed during all stages of growth, even if the intensity varied slightly. The complex forms, as it were, an essential component of the Panasqueira apatites.

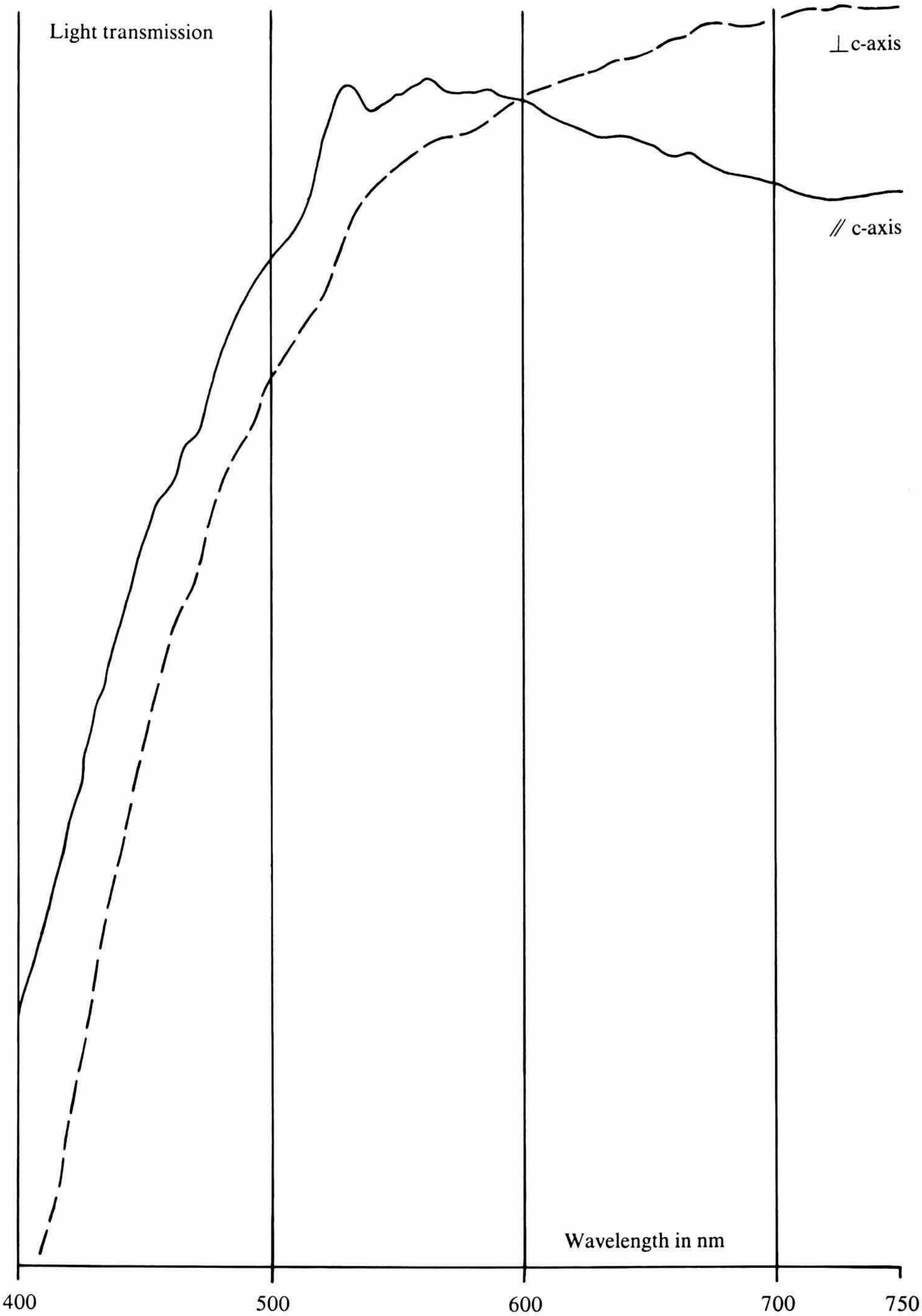

Fig. 4. Light transmission as a function of wavelength for the ordinary ray and the extraordinary ray in an apatite crystal, showing blue-green to yellow pleochroism. Solid line: 'B' complex, // c-axis; broken line: 'A' complex, ⊥ c-axis.

COMPARISON OF PLEOCHROISM OF THE PANASQUEIRA APATITES AND OF APATITES FROM OTHER DEPOSITS

Phenomena of pleochroism, remarkedly similar to the phenomena observed in the apatites from Panasqueira, are displayed with a high degree of intensity by the crystals of moroxite from the mines in the region of Sl'ud'anka, near the southwestern end of Lake Baikal in Siberia. These apatites, occurring in veins of muscovite, have been thoroughly investigated with different optical methods (Bachtin, Nizamutdinov & Vinokurov, 1972; Ščerbakova, Godovikov, Gilinskaja & Vasil'eva, 1970). Green crystals of apatite from Templeton, Ontario, Canada, of a short prismatic habit, also show the irregular distribution of the blue complex 'B' and the regular one of complex 'A'.

Next, the photograph of Plate 1, figure 1 shows the presence of areas of concentration of complex 'B' in both crystals from the Sauberg and from Panasqueira. Note the identical distribution. The photographs, reproduced on Plate 2, figure 2 are representing a long prismatic apatite crystal from Sl'ud'anka in light polarized parallel with the c-axis, and in light polarized perpendicular to the c-axis, respectively. The violet-blue colour with $\vec{E} \parallel c$ is especially striking. Plate 3, figure 2 shows the same phenomena in a crystal of apatite from Templeton, Ontario, Canada.

It is interesting to note here, that the apatites from Sl'ud'anka and from Templeton are notable for their very low concentration of manganese. These crystals do neither show the yellow luminescence, which can be ascribed to Mn^{2+}, nor are they phosphorescent. The concentration of lanthanide elements in both apatites is very low in comparison with the concentration in other apatites.

CONCLUSION ABOUT THE CAUSES OF THE OBSERVED PLEOCHROISM

In the foregoing part we have seen that the green apatites from Panasqueira, from Templeton, from Ehrenfriedersdorf, and the moroxites from Sl'ud'anka are exhibiting identical phenomena of pleochroism. Also, it has been demonstrated that the blue apatites from Panasqueira are not essentially different from their green counterparts; the blue colour is merely caused by a preponderance of the 'B' complex.

Types of apatite showing the blue complex colour with the highest intensity, such as the crystals from Sl'ud'anka, do not contain more than a few hundredth of a percent of manganese. In addition, manganese ions of normal valences do not cause absorption-maxima in the range near 720 nm (Bokša & Grum-Gržimajlo, 1970). It is therefore highly improbable that manganese ions would cause the intense blue colorations observed.

Several research workers have studied the chemical nature of the blue pleochroic complex in detail (Bachtin, Nizamutdinov & Vinokurov, 1972). They came to the conclusion that the visually observed blue colour is caused by a highly polarized absorption band with a broad maximum, centered around 710 to 730 nm. Destructive thermochemical experiments with the blue apatites of Sl'ud'anka proved that heating to a temperature of 430°C for several hours in air resulted in a complete disappearance of the blue colour. After the treatment, the absorption (or the transmission) curves in the directions $\vec{E} \parallel c$ and $\vec{E} \perp c$, were found to be identical and conform with the curve, characteristic for the yellow-green complex, 'A' in our case. Thus, this last complex is thermally much more stable than complex 'B'. The authors have come to the conclusion that the behaviour of the blue complex can only be explained by the existence of anisotropical lattice defects with a prefererential direction parallel to the c-axis of the crystal. Such defects can only be aligned with the F^{1-} anions or with the Ca^{2+} ions in ninefold coördination with oxygen. Here, the low thermal stability of the 'B' complex is reminiscent of the properties of electron deficiencies or 'holes', and the localization of these in halogen-ion sites in the apatite lattice. Furthermore, investigations with the EPR method demonstrated that the absorption-maximum in the neighbourhood of 720 nm can be occasioned by O^{1-} centres of electron-deficiency, interacting with the halogen-ions in their immediate vicinity.

Although our samples could not be subjected to thermal treatment in order to examine the stability of complex 'B', the properties of the complex observed in the apatites from Panasqueira are identical to those of the blue colour complex observed in the apatites from Sl'ud'anka. It is reasonable therefore to state that the blue colour in the apatite crystals from Panasqueira is very probably caused by O^{1-} electron-deficiencies in F^{1-} sites. This view is strongly supported by the observed peculiarities of the geometrical appearance of the zones of blue colour. These are indicative of actions of the environment on the crystal during periods of stagnancy of growth; the alterations could then develop from preferential loci on the exterior of the crystal.

The yellow-green colour of complex 'A' is caused by stronger absorption of the violet and blue rays, and in addition by several minor absorption-maxima in the wavelength-range extending from 585 nm to 655 nm. This is also visible in the transmissioncurves shown in Figure 4. The absorption in the blue and the orange-red regions must be ascribed to complexes of ions of manganese of different valences (Bokša & Grum-Gržimajlo, 1970), especially to the complex MnO_4^{1-} (Bachtin, Nizamutdinov & Vinokurov, 1972). The manganese ions of lower valences are replacing Ca^{2+} ions, and the complex anion MnO_4^{1-} can take the place of the PO_4^{3-} group. The weak polarization of the complex certainly is in accordance with this point of view.

In conclusion, it can be stated that the blue colour complex 'B' is best explained by the migration of O-ions to sites, where they settle as 'holes' in the halogen-ion chains during certain phases of crystal-growth. It is left to other researchworkers to study the thermal behaviour of this complex in detail; this may help to prove the validity of the explanation. The blue colour is certainly not caused by ions of manganese.

The yellow-green complex is ascribed to the presence of Mn^{2+}, Mn^{3+}, and Mn^{4+} ions in Ca^{2+} sites, and to the anions MnO_4^{1-} taking the place of the PO_4^{3-} groups. The presence of Mn^{2+} ions will be proved in the course of the next chapter. The occurrence of manganese ions of higher valences shows that in most stages of formation of the apatite crystals in the Panasqueira deposit the oxydation potential of the environment must have been high. The rose, or rather the red-purple or the blue-purple colorations, observed in parti-coloured crystals from Panasqueira are attributed to Mn^{3+} ions in Ca^{2+} sites.

Detection of trace elements by polarospectrographical analysis

In this chapter, the results of recent work on the analysis of trace elements in the apatite crystals from Panasqueira are brought to the attention of the reader. The analyses were made with the aid of a much improved spectrograph and source of radiation. Principles of the method and apparatus, which were developed for the specific purpose of non-destructive optical analysis of all sorts of crystallized substances will not be explained in detail; they have already been described in earlier publications (Lagerwey, 1973, 1974 a, b). Spectrophotograms are reproduced showing highly resolved structures of groups of absorption and luminescence lines. These photographs do not only show the unrivalled power of resolution of photographic registration, but they are a demonstrative proof of the feasibility of the detection and identification of the very smallest concentrations of ions of rare elements, such as Eu^{3+}, by their luminescence spectra. The results thus obtained, are certainly original and unexpected, if one is to judge from the trend of current publications on the subject in some well known periodicals.

GENERAL DESCRIPTION OF METHODS SELECTED

Three main methods of research were used in the experiments, which will be described in this section.

In the first place, polarized absorption line-spectra were photographically recorded in the infrared and visible ranges of the spectrum, combined into a continuous range from 1000 nm down to 400 nm. The spectra were generated by flooding the crystal to be examined with continuous light of a wavelength-range, corresponding with the range of registration. The light, re-emitted by the crystal, was analyzed with a three-prism spectrograph, provided with high qualitity polarizing equipment, including a compensator for the neutralization of polarization effects, proper of the spectrograph. The line groups in the polarized spectrophotograms thus obtained, were compared with standard absorption line-spectra of synthetic fluorapatites, doped with known concentrations of trace elements normally occurring in apatite. In this way, the identity of the lines could be established with certainty. The intensities and wavelengths of individual lines could be measured, the latter with great accuracy, for the purpose of structural analysis of the spectra. From the data obtained, conclusions were drawn about the nature of the ions present, their concentration, and about the crystalfield in the vicinity of the ions.

In the second place, the excitation-characteristics of the crystals having been evaluated, luminescence line-spectra were registered in the same wavelength-ranges as the absorption spectra. Luminescence in the crystals was excited by an intense beam of continuous light, focussed on their surface. The wave-length-passband of this beam was adjusted with the help of filters to the characteristics of excitation of the ions to be analyzed. The light, re-emitted by the crystal, was then filtered to remove the excitation-waveband from the emissions of the active ions, and analysed with the spectrograph and polarizing equipment as mentioned before. The spectrograms obtained were next compared to standard luminescence line-spectra of synthetic fluorapatites in order to identify the active ions. The determination of wavelenghts and line-intensities in the spectra with $\vec{E} \parallel c$ and $\vec{E} \perp c$ completed these measurements. From the results, data were obtained about the identity of the active ions, their concentration, and about the crystalfield in the vicinity. The luminescence analysis is extremely useful, as there are a number of lanthanide elements which do not possess distinctive absorption lines in the considered ranges of wavelength, but which do show characteristic luminescence (Blasse & Bril, 1970). Also, there are some ions of transition elements (metals of the A-subgroups of groups V, VI and VII, and the metals of group VIII of the periodical system of the elements; see Hubbard, 1969), such as Cr^{3+} and Mn^{4+}, which can be analyzed by their line emissions (Lagerwey, 1974b).

In the third place, spectrophotometric measurements were conducted in order to determine the wavelengths of maxima of broad luminescence bands, which may be caused by ions of the transition-metals, bivalent lanthanides and heavy metals. These maxima can reveal the identity of the ions, if their characteristic maxima are known. Analysis of the excitation-spectra of the apatite crystals is very useful here (Harber, Nikitina, Sotnikov & Ščerbakova, 1970).

Lastly, a number of tentative experiments were carried out to explore the nature and causes of strong phosphorescence, noted in a number of apatite crystals from Panasqueira.

ABSORPTION-SPECTOGRAPHY; ANALYSIS OF LINE-SPECTRA

In the course of preliminary investigations carried out with a spectrometer, typical groups of absorption lines, caused by trivalent neodymium, could be identified in the samples S. 362 and S. 363. The neodymium content of crystal S. 248 and of the apatite crystals in sample RGM 251 424 proved to be too low to make detection by absorption possible.

Neodymium in the trivalent state generates systems of rather sharp absorption lines in different ranges of wavelengths, such as 806 - 796 nm, 763 - 734 nm, 610 - 565 nm, 532 - 516 nm and so forth. Many of the lines are totally polarized in crystals of apatite.

The varying structures of the groups of lines caused by Nd^{3+} were studied intensively during several years; about seventy different apatites from many different types of deposit were analyzed. The spectrograms of the neodymium lines did show such systematical configurations of lines in each group, that it proved to be possible to distinguish a rather small number of characteristic spectral types of apatite. The characteristic configurations of lines are obviously caused by systematic configurations of the crystalfield in the vicinity of the Nd^{3+} ions, taking the place of Ca^{2+} ions. Compensation of the excess space charge is an important variable here. Because of time and economics involved in the research, the group of neodymium lines in the range between 610 and 565 nm has generally been used in the work of classification. Of course, the other groups of absorption lines do show the same characteristic configurations and it will be demonstrated that the configurations, observed in the group of luminescence lines of Nd^{3+} near 876 nm, show the same particularities.

The polarized absorption spectra of crystal S. 362 are reproduced in Figure 5. The first (Fig. 5a) shows the spectrum polarized perpendicular to the c-axis; the second (Fig. 5b) shows the spectrum polarized parallel with the c-axis. The shorter bright lines in the centre are emissionlines of neon and mercury, which can be used for the purpose of calibration. The spectrograms are clearly showing the uncommon sharpness of the Nd-lines, and the very pronounced polarization-effects. From this, it can be concluded that the Nd^{3+} ions in the lattice of crystal

S. 362 are located in regular and identical sites, and that the crystal is of considerably purity.

From the density of the main absorption lines of Nd^{3+} and by comparison with standards, it was calculated that the concentration of Nd in crystal S. 362 is 110 ppm ± 10 ppm (parts per million, or milligrams per kilogram). This is a relatively low concentration in comparison with the concentration of Nd observed in the well known yellow crystals from the Cerro de Mercado in the state of Durango, Mexico: the crystals from the author's collection show an average content of 900 ppm. Data published about the concentration of lanthanides in minerals should be handled with care. This becomes painfully clear, when the reader reviews the current litterature about the composition of the wonderfully clear and homogeneous apatite crystals from the Cerro de Mercado (Brunfelt & Roelandts, 1974; Young, Myers, Munson & Conklin, 1969): almost any analysis resulting in different values for the concentration of one element. Of course, it is clear that the composition of individual crystals from one site can greatly vary. This is certainly the case with the apatites from Panasqueira.

According to data published about the average concentration of neodymium in rocks forming the crust of the earth (Gmelin, 1938; Mason, 1952), this so-called Clarke concentration is of the order of 24 ppm (or 24 grams per ton). Therefore, the factor of enrichment, defined as the quotient of the concentration of an element in a mineral and the Clarke-concentration, is about 4.6 for neodymium in crystal S. 362.

In order to be able to appreciate the differences in the structure of the multiline-absorptions caused by the ion Nd^{3+} in different types of apatite, the polarized spectra $\vec{E} \perp c$ and $\vec{E} \,/\!/\, c$ of an apatite crystal from Cerro de Mercado are reproduced in Figure 6a and b, respectively. If these spectrophotograms are compared with Figure 5a and b, the inevitable conclusion must be that the crystalfield in the vicinity of the Nd^{3+} ions in the lattice of each crystal is distinct. It can be proven that the overwhelming majority of the yellow apatites of long prismatical habit, formerly named 'asparagus-stone' or 'aspergolite', are exhibiting the same multiline-structure of Nd^{3+} as observed in the apatite from the Cerro de Mercado. Definite examples are the apatites from Jumilla, Murcia, Spain; from a deposit in Cumberland, England, and from the island Hurmuz in the Persian Gulf. These apatites are essentially fluorapatites, just like the crystals from Panasqueira. This justifies the conclusion that it is indeed possible to classify apatites by the particularities of their lanthanide spectra. The method is of practical value, as very many apatites do contain enough neodymium to show the tell-tale absorption spectrum (or the infrared luminescence spectrum). It will be noted that apart from the entirely different Nd-linepattern, in the given wavelength-range, the absorption lines of the apatite from Cerro de Mercado are much more diffuse than those proper of the Panasqueira apatite. Still, they are relatively narrow — if one considers the rather large dispersion of 6 Å per mm of the spectrophotograms — and well defined. This rather contrasts with the opinions, expressed by other researchers, who have studied the apatites from the Cerro de Mercado in extenso saying, that only some weak and broad absorption bands can be observed (Young et al., 1969). The specific differences in the structure of the neodymium-spectra, the reality of which is proved by the spectrograms first published in this article, also stand in clear opposition to statements about the crystalchemistry of apatites containing 'rare earth' ions, such as the ones pronounced by Grisafe and Hummel: 'The reflectance spectra (of apatites, containing praseo-

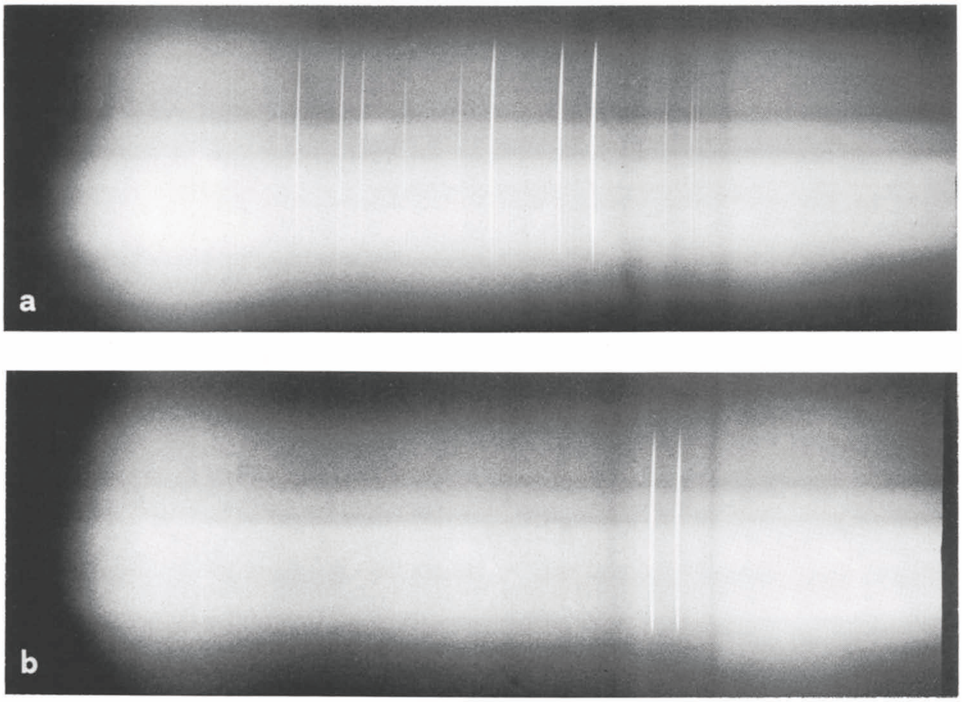

Fig. 5. Absorption spectra of Nd^{3+} in crystal S. 362; a: polarized perpendicular to the c-axis; b: polarized parallel with the c-axis.

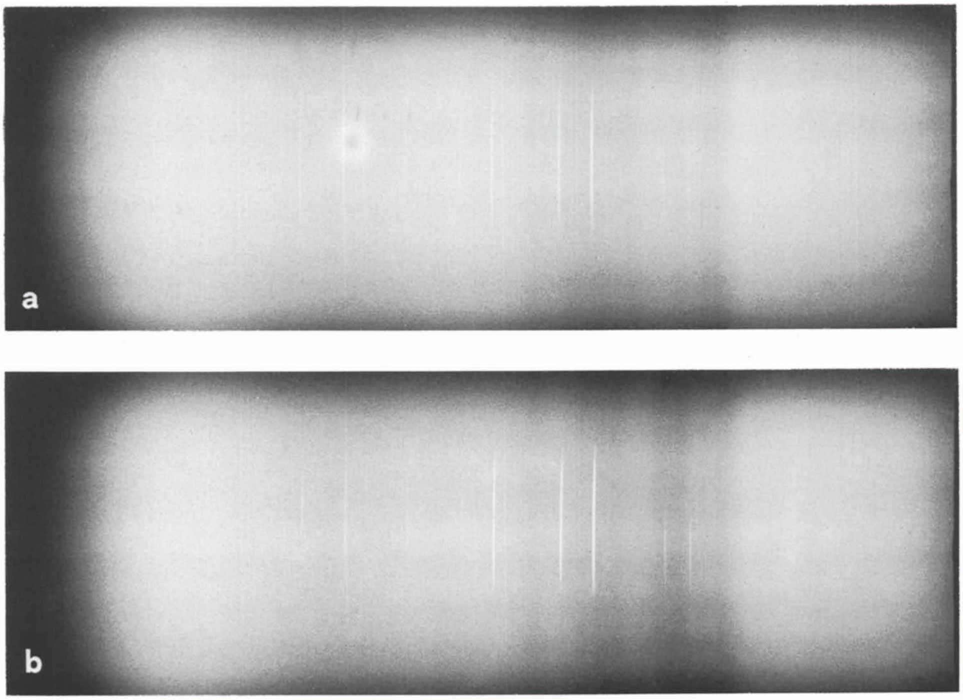

Fig. 6. Absorption spectra of Nd^{3+} in a yellow apatite crystal from the Cerro de Mercado (Mexico); a: polarized perpendicular to the c-axis; b: polarized parallel with the c-axis.

dymium and neodymium) were similar to the reflectance spectra of the praseodymium and neodymium oxide' (!), and: 'The positions of the absorption maxima for a given rare earth ion are not affected by the composition (including defects) of the host apatite' (Grisafe & Hummel, 1970). These facts are certainly proof of the value of the new method, which is capable of revealing effects which were hitherto unknown, or unexplored.

Our findings regarding the concentration of neodymium in S. 362 were confirmed by subsequent analysis of the luminescence spectrum of Nd^{3+} in the near infrared region. S. 363 possesses an absorption spectrum which is identical with the spectrum of S. 362.

By means of a statistical study performed with the aid of an extensive collection of more than 400 absorption spectra, which were recorded of the different apatites from the collection mentioned on page 19, it was demonstrated that four types — at least — of fine-structures of the neodymium spectra could be distinguished. To demonstrate this, the particularities of the polarized spectra of representative samples of these four classes of apatites are represented in the diagrams, reproduced in Figures 7 and 8. In Figure 7, the spectrum of crystal S. 362 from Panasqueira and the spectrum of a pink-coloured fluorapatite from Fellen-St. Goar (FRG) are shown in opposition. The wavelength-range of the diagram lies between 568.00 nm and 592.50 nm; the polarization and the intensity of each line are indicated. In Figure 8, the spectrum of the yellow fluorapatite from the Cerro de Mercado is compared with the spectrum of a F-Cl apatite from the Zillertaler Alps in Austria. These diagrams show that the differences, which were used for distinction, are quite notable. It will be seen that the apatite from Panasqueira belongs to a separate class, which has several important lines in common with the apatite from the class of the St. Goar apatite. These two classes are related. It is a fact that both are notable for their europium spectra. On the other hand, the spectral types, shown in Figure 8, differ considerably from those, shown in Figure 7. It can be concluded that the crystalfield in the vicinity of the Nd^{3+} ions in the apatite crystals from Panasqueira is similar in a higher degree to the field proper of the pink apatites (represented by the apatite from St. Goar), and that it differs from the fields proper of the two types of yellow apatite, these being quite different from each other.

The compilation of data, necessary for this sort of classification, is a voluminous task. Also, a very high degree of accuracy of measurement is required for the establishment of relations between the different types of spectrum. The electro-optical systems, generally used for the registration of spectra, will never suffice for this type of work. Only photographic registration has sufficient possibilities of resolution and accumulation. It should be understood that the work, some results of which are reported in this article, is not yet rounded-off completely. A monograph on the subject will be published in due course.

The line-structure of the Nd^{3+} absorptions has been demonstrated to be a good indicator of modifications of the crystalfield in the vicinity of the neodymium-ions, replacing the calcium-ions of different coördination in the apatite structure. One would rather expect, in consequence, that the Nd spectra of all apatites would be different, showing many subtle differences in line intensities, wavelengths, and directions of polarization. It is therefore really surprising that but a few distinct line patterns are observed, especially as it is realized that apatites of one and the same spectral type may show rather important variations in chemical composition.

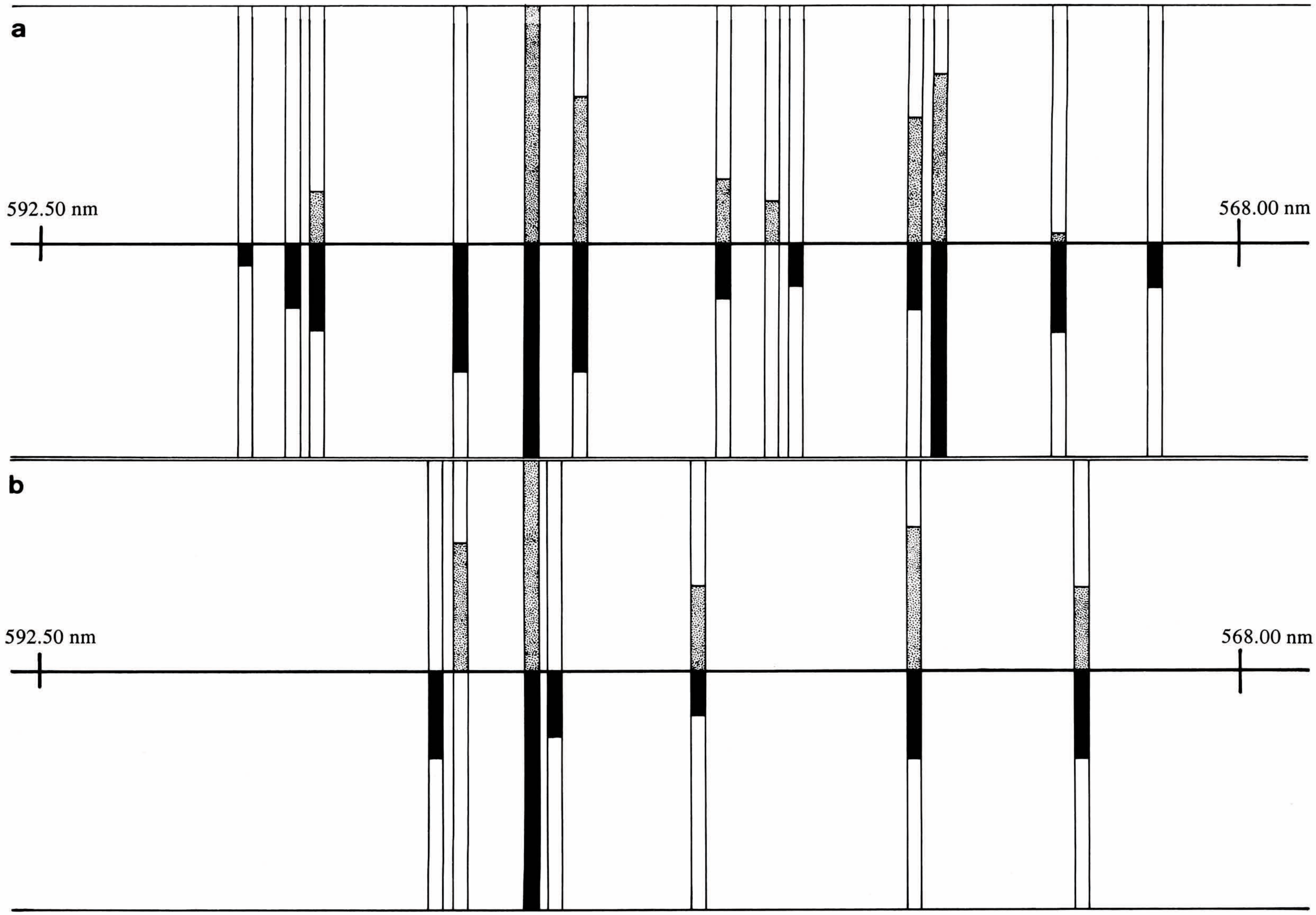

Fig. 7. Diagrammatical representation of the polarized absorption spectra of Nd^{3+} in fluorapatites, wavelenght range between 568.00 and 592.50 nm; a: from the Panasqueira Mine (Portugal), sample S. 362, const. type D-1; b: from Fellen-St. Goar (FRG), sample S. 175, const. type A-1. Dotted (above the horizontal lines): intensity of absorption lines with light polarized perpendicular to the c-axis; solid black (below the horizontal lines): intensity of absorption lines with light polarized parallel with the c-axis.

It is not as yet possible to give an acceptable explanation of the appearance of the typical spectral structures. Here, it may be of interest to note that the apatites, belonging to the same spectral group, show a remarkable resemblance in external appearance and colour. It would be justified even to replace the term 'spectral type' by 'constitution type'. The old idea of linking crystal habits and colours with certain types of deposits and parageneses is raising its head again!

For instance, apatite crystals of the spectral 'A' type are all of a very light rose-red to flesh colour, very different from the lilac colours observed in apatites from pegmatites or from veins of the Alpine type. All crystals are of flat tabular habit; they consist of nearly pure fluorapatite. Examples of sites are: Fellen-St. Goar (FRG), a certain deposit in the vicinity of the Lukmanier Pass in Switzerland, Morro Velho in the state of Minas Gerais in Brasil.

The apatites, belonging to the 'B' type, are all of long prismatic habit with well developed pyramids. Their colour varies from straw-yellow to rosin-brown; pleochroism is usually very weak or absent. Typical deposits are: Cerro de Mercado in Mexico, Jumilla in Spain, a certain deposit in Cumberland, England, the island of Hurmuz in the Persian Gulf, Batg in Iran, etc.

The apatites, belonging to the 'C' type mostly are of a rough hexagonal shape. The colour varies from yellow-green to brownish-yellow. The chlorine content is appreciable. Luminescence is very weak, probably as a consequence of the presence of quenching ions, such as Fe^{3+}. Examples of sites are: a deposit on the mountainmassif of the Grosser Greiner in the Zillertaler Alps, Austria; Bamle in Norway; etc.

The 'D' types of apatite show a pronounced short prismatic habit with well developed basal pinakoids. Longer prismatic crystals are also common. The colour is usually a very light grey-green to dark-green. The presence of areas showing a blue pleochroic colour with $\vec{E} \parallel c$ is typical. The concentration of lanthanide elements is low: they are only enriched in a minor degree in respect to the Clarke concentration. Typical sites are: Panasqueira in Portugal, Ehrenfriedersdorf in Saxony (GDR), Horní Slavkov in the ČSSR, etc.

The apatites of the Alpine type form a class apart. Here, the concentrations of the usual trace elements are extremely low. Even the content of neodymium proved to be too low, until now, to allow a precise classification of their types. They could be qualified for reason of their purity, as 'empty apatites'. The colour is usually water-white to light mauve with a violet tinge. The crystals are perfectly developed, of short prismatic habit, showing very many faces.

As the present article mainly intends to introduce discoveries, which can be made with the polarospectrographical method of analysis, we will refrain from giving more detailed considerations.

LUMINESCENCE-SPECTOGRAPHY, ANALYSIS OF LINE-SPECTRA

In view of the complicated and multiple processes of energy-transfer possible between groups of different ions of various trace elements, which ions can act as sensitizers or as activators, very precise methods had to be devised for the analysis of elements, active in the Panasqueira-apatites (see Blasse & Bril, 1970; Bril, Blasse, Gomes de Mesquita & de Poorter, 1971; Bachtin & Mashonkin, 1972). Of crucial importance here was the optimal and selective excitation of the lanthanide elements. The results of the extensive experiments are shown in a

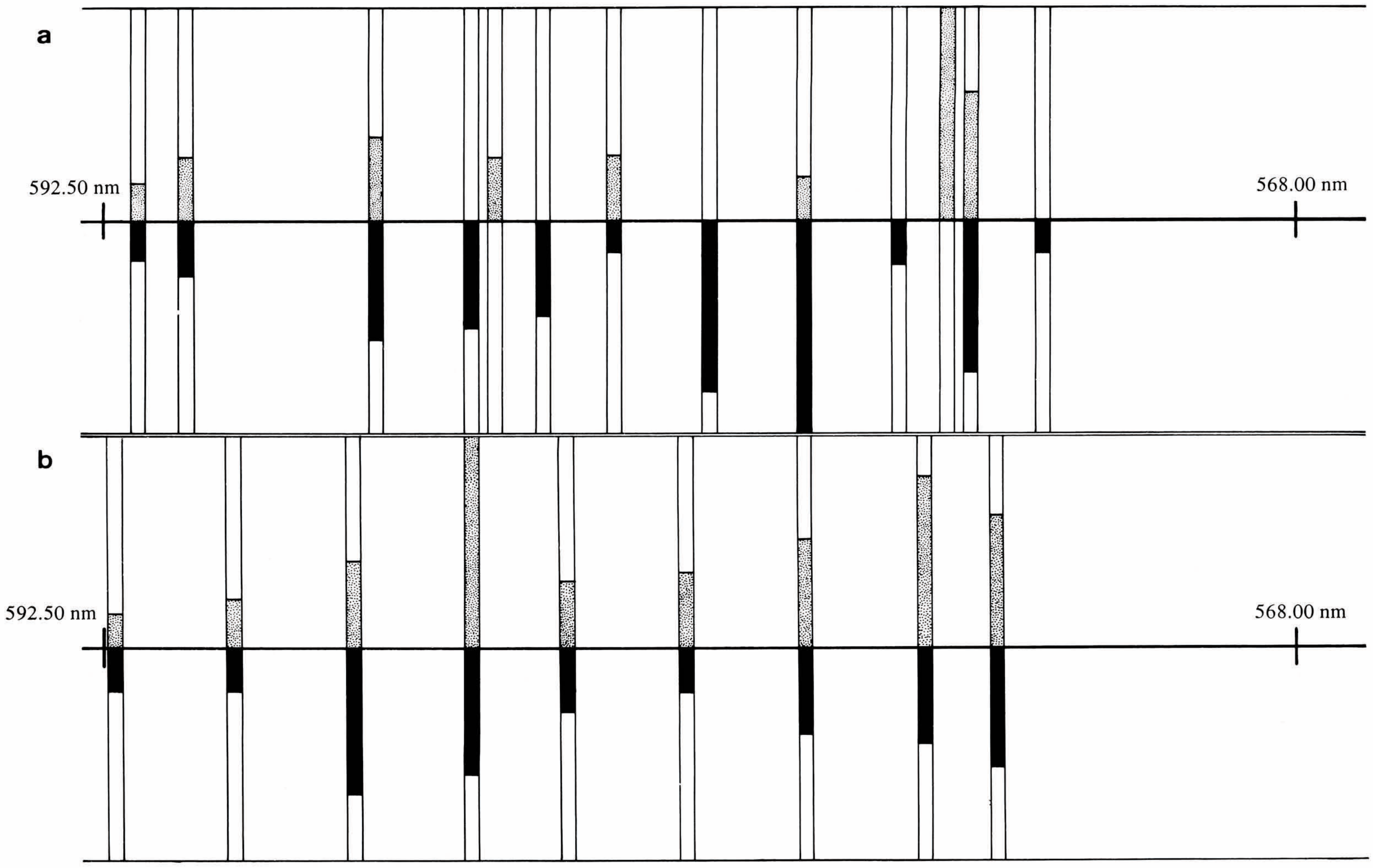

Fig. 8. Diagrammatical representation of the polarized absorption spectra ofNd^{3+} in apatites, wavelenght range between 568.00 and 592.50 nm; a: from Cerro de Mercado (Mexico), sample S. 145, const. type B-2; b: from the Grosser Greiner (Zillertal, Austria) F-Cl apatite, sample S. 245, const. type C-1. Dotted (above the horizontal lines): intensity of absorption lines with light polarized perpendicular to the c-axis; solid black (below the horizontal lines): intensity of absorption lines with light polarized parallel with the c-axis.

number of spectrophotograms, which were recently registered and which are published here for the first time. Figure 9a shows the luminescence lines of trivalent europium in a synthetic fluorapatite in the wavelength-range between 640 nm and 560 nm. The average dispersion of the spectrum is about 6 Å per mm. High energy photons were used for the excitation. Figure 9b shows a spectrophotogram of the same synthetic fluorapatite, in the same range of wavelengths. Here, photons of much lower energy in the neighbourhood of 3.0 to 3.5 eV were used. It will be remarked, when the Figures 9a and b are compared, that the character of the lines and their intensities are sometimes different. As both spectrophotograms were made from one and the same sample, it is evident that the composition of a luminescence spectrum is influenced by the mode of excitation employed.

Figure 10 shows a spectrogram of the fluorapatite crystal S. 362 from Panasqueira in the same range of wavelengths, excited selectively by a flux of high-energy photons. The selectivity of the excitation is demonstrated by the fact that only the ion Eu^{3+} was excited: all sixteen lines or so originate from this ion. In contrast, Figure 11a shows a spectrogram of the same crystal under full excitation with blue radiation in the wavelength-range, reaching from 400 nm to 500 nm (photon-energy between 2.5 and 3.1 eV). The luminescence lines are polarized parallel with the c-axis. The main emissionline of Eu^{3+} in fluorapatite (Fap) is still clearly visible amidst the lines caused by Pr^{3+}, Sm^{3+} and Dy^{3+}. The spectrogram of Figure 11b was taken under identical conditions, only the rays are polarized perpendicular to the c-axis in this case. The calibration-lines were generated by a caesium-source.

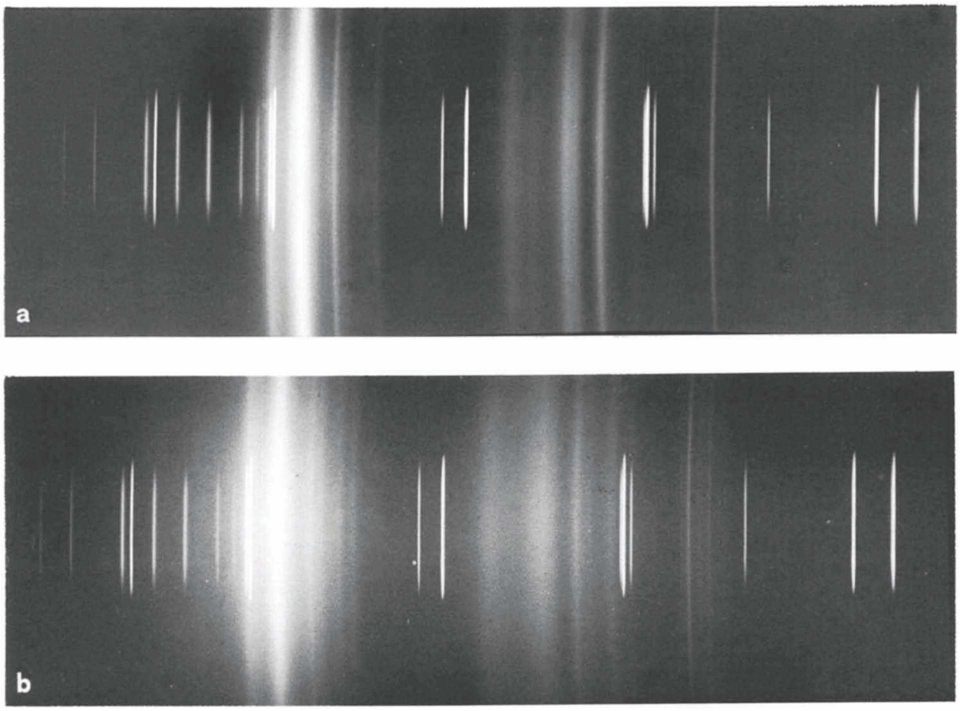

Fig. 9. Luminescence lines of Eu^{3+} in a synthetic fluorapatite, in the wavelenght range between 560 and 640 nm. The spectrum is excited a: by photons with an energy higher than 3.5 eV; b: by photons in the energy range between 3.0 and 3.5 eV.

The established media of publication, reserved for the domain of crystal-chemistry and physics, are frequently reporting on the extreme weakness of the emissions of Eu^{3+} ions: 'a thousand times or more' weaker than the emissions of Eu^{2+}, and of 'the impossibility of the appearance of lines from Eu^{3+} in the luminescence spectrum of apatite' (Bachtin & Mashonkin, 1972). The original and objective photographic evidence, which is published in the present article and which proves that lines of Eu^{3+} can be prominent in the luminescence spectra of fluorapatite, stands in clear contrast to these cited opinions, which are based solely on theoretical considerations. The necessity of conducting experiments, even with the aid of unconventional techniques and without being prejudiced by bare theories, is evident.

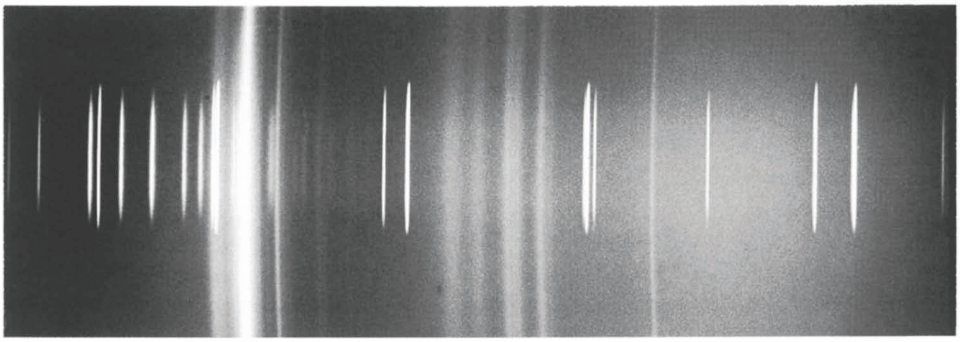

Fig. 10. Spectrophotogram of the apatite crystal S. 362, showing exclusively the characteristic luminescence lines of Eu^{3+}. The selective luminescence was excited by photons of an energy higher than 3.5 eV.

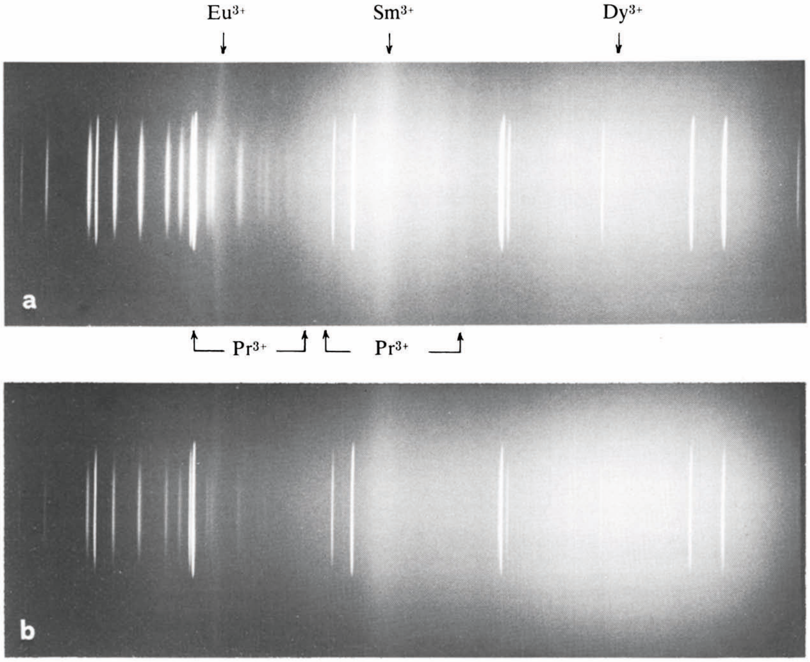

Fig. 11. Spectrophotograms of the general luminescence of crystal S. 362, in the range between 560 and 640 nm, excited by blue radiation; a: the electric vector is directed parallel with the c-axis; b: the electric vector is directed perpendicular to the c-axis.

The lines, proper of the ions Pr^{3+}, Sm^{3+} and Dy^{3+}, could be identified with the aid of spectrograms of synthetic fluorapatites. These spectrograms are all of the same quality as the ones shown in Figure 9. The spectrogram, reproduced in Figure 12a shows the luminescence spectrum of S. 362 in the near-infrared region between 720 nm and 920 nm: the characteristic lines of Nd^{3+} and Pr^{3+} are present. The same spectrum could be observed in sample RGM 251 424; the apatite crystals in this sample are representative of the whole generation of this mineral formed in the muscovite selvages. The possibility of the emergence of the luminescence lines of trivalent praseodymium has also been called in question (Bachtin & Mashonkin, 1972, p. 61) on grounds of the higher probability of energy-transfer to other ions. Nevertheless, the Pr^{3+} lines are well represented in our spectrophotograms.

In other spectrograms, which cannot be reproduced here because of restrictions of space, faint traces of the characteristic lines of Tb^{3+} in the Fap-lattice could be observed.

It is really surprising that since the exploration work by Haberlandt, 1938, Köhler (in Köhler & Haberlandt, 1935) and Iwase (1935) on the luminescence spectra of apatites from various types of deposit, till recent times, practically no progress was made in the field of production and analysis of discrete line spectra, exhibited by mineral apatites. Haberlandt obtained luminescence linespectra of lanthanides only after calcination of the samples, but in this case the structure of the material must have been changed irriversibly. Still, the high quality spectrograms, which are reproduced here, could be obtained with relatively simple equipment and at no great expense.

Just as in the case of the absorption line-spectra, the luminescence line-spectra are showing distinct patterns of lines in groups, characteristic of an active ion. Here also, it is possible to distinguish various types of apatite by means of their characteristic line-patterns. As it is reasonable to expect, apatites, displaying the same absorption line-patterns, are also showing similar patterns of luminescence lines. The spectacular nature of differences in appearance of line-spectra will be appreciated if one compares the luminescence spectra of Nd^{3+} in the infrared region of crystal S. 362 from Panasqueira (Figure 12a) and the spectrum of a typical yellow crystal of apatite from the Cerro de Mercado (Figure 12b). The obvious conclusion seems to be that the configuration of the crystalfield in the vicinity of the neodymium ions is different in both types of fluorapatite. This difference may well be a consequence of the very different geochemical characteristics of the Panasqueira-deposit and the deposit in the Cerro de Mercado (described in Foshag, 1929; McConnell, 1973; Young et al., 1969). The spectrograms show the same sort of compositional difference, which arises as a consequence of different intensities and different character (sharp, diffuse, etc.) of particular lines, as can be observed in the absorption spectra. To cover all active elements, both techniques have to be used in combination.

Indications of the presence of the heavier lanthanide elements holmium, erbium, thulium and ytterbium could not definitely be detected in the Panasqueira apatites sofar. Thus it seems that the concentration of these elements in the crystals of apatite must be equal to, or lower than their respective Clarke-concentrations.

From the comparative intensities of the main luminescence lines, proper of the ions Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, and Dy^{3+} under specific conditions of excitation in respect to the corresponding line intensities, observed in standard Fap

preparations, it was possible to make a reasonable estimation of the concentration of these ions. Several groups in different ranges of wavelength were considered, and in the case of neodymium, the results could be compared with data obtained from the absorption spectra. The results are as follows:
Pr^{3+} — 11 ppm; Nd^{3+} — 110 ppm; Sm^{3+} — 55 ppm; Eu^{3+} — 10 ppm; Dy^{3+} — 25 ppm.
The concentration of praseodymium is very low in respect to the concentration of neodymium, samarium appears to be enriched, and the concentration of europium is relatively high. The dysprosium concentration is practically normal. Elements, like samarium, europium and ytterbium are also appearing in a bivalent state. These bivalent ions give rise to broad luminescence bands, which must be analysed in a different way:

ANALYSIS OF BROADBAND LUMINESCENCE SPECTRA

For the global analysis of the broadband luminescence spectra, which can be excited in the apatite crystals from Panasqueira, direct spectrophotometry was used to determine wavelengths and intensities of maxima. These determinations had to be limited to the visible range of the spectrum (approximately situated between 390 nm and 760 nm).

It is interesting to make a few notes on the visible colour of the luminescence-light emitted by the crystals, observed when the mode of excitation is being

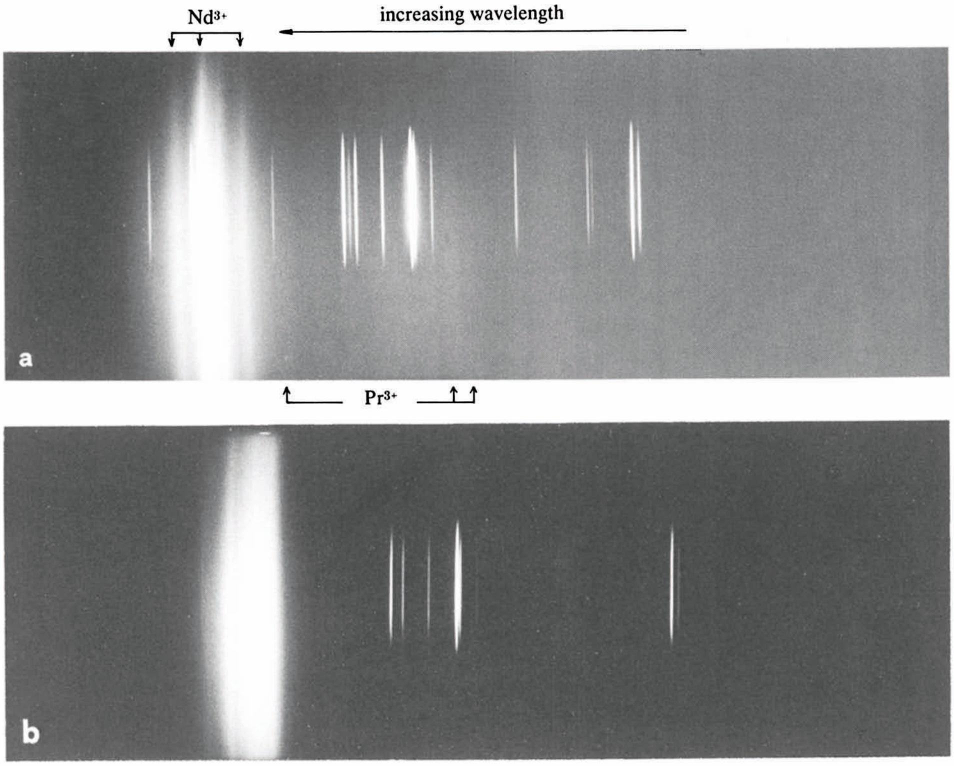

Fig. 12. Spectrophotograms of luminescence in the infrared range of wavelengths from 720 to 920 nm of: a: crystal S. 362 from Panasqueira, showing the lines of Nd^{3+} and Pr^{3+}; b: crystal S. 145, yellow apatite from the Cerro de Mercado, Durango, Mexico; the structure of the main group of Nd^{3+} lines should be compared to the same in spectrophotogram a.

varied. We will treat sample S. 362 as an example: under excitation with blue-green or blue radiation, the colour of the luminescence observed is interpreted as an intense orange-red; the maximum of intensity occurs at a wavelength of 580 nm. When the wavelength of excitation is decreased, the colour changes to yellow. Under excitation with shortwave ultraviolet radiation (4.9 eV) the colour generally looks mustard-yellow. In other crystals, this ultraviolet radiation excites an intensely sky-blue luminescence in basal layers of a few millimetres thickness. The luminous flux, excited by high energy photons, exhibits not only a maximum of intensity near 580 nm, but also a wide maximum which seems to shift from 450 nm to 430 nm when the photon-energy is increased, Another, minor, maximum seems to be present at some wavelength shorter than 400 nm. The exact wavelength of this maximum could not be determined. The intensity of both maxima in the violet region increases in proportion with the energy of the photons which excite the luminescence. Changes in colour, as observed by the eye, are thus caused by changes in relative intensity of the different maxima and not by a shift in wavelength of the maxima. The only sort of shift observable is an apparent one, caused by the additive effect of the overlapping wide bands.

The type of broadband luminescence, which is described here for apatite from Panasqueira, has also been observed in apatites from various kinds of deposit by many authors (Iwase, 1935; Harber et al., 1970; Bachtin & Mashonkin, 1970). Iwase shows spectrograms of apatite from Ehrenfriedersdorf (tin-tungsten paragenese), from Quebec (Canada), and from some Japanese deposits. Harber et al. show excitation and luminescence spectrograms of apatites from granites and greisen veins in the Altai Mountains, and Bachtin produces spectrograms of apatite from Ehrenfriedersdorf, from the Greiner in Austria, from pegmatitic deposits in the Urals, and from the apatite mountain near Lovozero, Kola Peninsula.

It is useful to observe, that the spectrograms of the broadband luminescence in the range of wavelengths considered do not convey information about a large complex of variables, such as the line spectrograms do. Instead of wavelengths, intensities and polarization of several groups of lines, each of which may consist of tens of lines, we see only a few, very broad maxima, with weak effects of polarization. Shifts, measured in the wavelengths of the maxima, are usually insignificant in respect to the bandwidths. It is, therefore, not surprising that efforts to employ the characteristics of broadband luminescence for the classification of apatites in relation to their parageneses did not yield really significant results. This is underlined by the negative results of the method of classification of apatites by their broadband spectra, reported by Bachtin (Bachtin & Mashonkin, 1972). In vivid contrast to this, the method of distinction of types of apatite proposed in this paper is based on characteristic assemblies of many variables determined with the aid of line-spectra and broadband-spectra. It seems predestined to yield much more significant results: its 'resolving power' is much greater. For the development of the method, however, extensive studies and numerous observations are required. The results, when properly treated statistically, could well lead to a revision of many notions concerning the structure of apatites considered in relation to their formation.

A detailed consideration of the excitation-characteristics of broadband luminescence shows that these characteristics are practically identical for each observed luminescence band. This means that one distinct group of ions acts as activator of total luminescence. The sensitizer-ions absorb the incident radiation

— without subsequent emission — and transmit the energy absorbed to other active ions, called activators. These ions will absorb the energy first (excitation) and thereafter radiate this energy in characteristic quanta. In the case of the Panasqueira apatites studied, it is possible to state that the maximum around 580 nm is caused by Mn^{2+} activator-ions and the maximum around 450-430 nm by Eu^{2+}. Ions of Ce^{3+} are probably acting as non-radiative sensitizers. Cerium is nearly always present in considerable concentrations in most apatites, the average concentration being of the order of 3000 to 6000 ppm or more.

To sum up our conclusions: the Panasqueira apatite contains Mn^{2+} ions which are replacing Ca^{2+} ions, as well as ions of manganese of higher valences mentioned in the chapter about pleochroism. In addition, ions of Eu^{2+} are present, also replacing Ca^{2+} ions. In some crystals of a special type, these europium-ions are concentrated in basal layers, as we have already indicated. These layers are usually completely colourless (absence of interfering centres), while the body of the crystals shows a blue-violet colour. The intensity of the luminescence caused by shortwave ultraviolet rays is notable, but the actual concentration of Eu^{2+} is exceedingly small, such as is the case with fluorspar, which normally shows this characteristic blue luminescence. The great intensity is mainly a consequence of high probability of occurrence of the processes of energy transfer involved. The concentration of Eu^{2+} in normal crystals of apatite from he Panasqueira deposit like S. 362, or in crystals in a composite sample like RGM 251 424 is rather difficult to estimate, but will not exceed one thousandth of a percent (10 ppm). The concentration of Mn^{2+}, on the contrary, can be estimated quite accurately from the intensity of the characteristic maximum of luminescence at 580 nm: it is calculated to be 0.2 % weight in crystal S. 362.

We are now coming to the last paragraph of this paper, which will be dealing with phosphorescence effects, which can be observed in many apatite crystals from the Panasqueira deposit. The phosphorescence is closely connected to the complexes, which are causing the broadband luminescence.

PHOSPHORESCENCE: OBSERVATIONS AND TRENDS FOR FURTHER INVESTIGATIONS

Strong phosphorescence was observed in many crystals of apatite from Panasqueira directly after exposure to the concentrated flux of blue or violet radiation required for the registration of luminescence spectra. In many cases, the threshold level of intensity for the perception of colour by the eye was exceeded, and the colour of the emitted light was observed as being yellow-green. The same yellow-green emission was also noted in earlier experiments with apatite crystals from other deposits which had been exposed to cathode-rays of 100 keV. The decrement of intensity of the phosphorescence with time was relatively low (long 'half life'), and the light remained visible for more than half an hour in some cases. The phosphorescence could also be 'frozen in' and released by posterior heating (thermoluminescence).

A series of experiments was arranged for a preliminary survey of the effects of phosphorescence. For the excitation of phosphorescence, the crystals were exposed to pulses of light emitted by a xenon-flashtube. The peak intensity of radiation is reached at a wavelength of 520 nm (colourtemperature about 5600°K). The peak power per pulse of 15 Joule could reach about 30 kW. The building-up of the intensity of phosphorescence to a maximum could be studied by exposing the crystal to a varying number of pulses in rapid succession. The decay of the phosphorescence was determined by observation of the intensity of the emitted light as a function of time. The characteristics of the phosphorescence observed could then be related to particularities of the crystals; with the following results:

Maximum peak-intensities and long half-life periods of phosphorescence were noted in a crystal of a bluish-violet colour having water-clear basal layers (0001) of about 2 mm thickness. It is of the same type as the crystals, mentioned in the previous paragraph, showing the intensely blue luminescence which is characteristic of Eu^{2+}. The phosphorescent centres appear to be concentrated in these basal layers. Analysis of the light indicated a maximum of intensity at a wavelength of 550 nm. The halflife period was of the order of one minute and the light remained visible to the adapted eye for more than 15 minutes.

The clear green crystals with blue, diffused pleochroic zones — of which class crystal S. 362 is an example — all show notable effects of phosphorescence, even if the intensity is much lower than in the case of the crystals mentioned in the previous section. The period of halflife is of the order of several seconds and the period of visibility to the adapted eye is limited to one minute at most. The phosphorescence is again concentrated in the clear parts of the crystal, near the pyramidal endfaces.

Light-green parti-coloured crystals with red- or violet-purple outer prismatic zones do not seem to exhibit perceptible effects of phosphorescence. An example of this type of crystal is shown on Plate 4, figure 1.

The blue crystals of aggregate S. 363, shown on Plate 1, figure 2, are exhibiting phosphorescent centres, which are concentrated in the planes of contact indicated in Figure 3. The phosphorescence is of medium intensity; the period of halflife is of the order of three seconds and the period of visibility to the adapted eye varies from 30 seconds to one minute.

The complex observations can be characterized as follows:

Phenomena of phosphorescence and thermoluminescence are observed in most types of apatite crystals from Panasqueira. Phosphorescence is particularly pronounced in the clear basal (0001) layers of crystals, showing a blue or violet bodycolour. These crystals are sometimes capped by clusters of crystals of secondary pyrite. These phenomena are also observed, albeit in a lesser degree, in very light green and clear crystals which exhibit the blue pleochroic 'B' complex in areas of diffusion. Phosphorescence is very weak or imperceptible in the generation of flat prismatical parti-coloured crystals.

The waveband of phosphorescence (and of thermoluminescence) is centered around 550 nm and extends from 525 nm to 575 nm approximately. In comparison to the broadbands with maxima near 580 nm and 450 - 430 nm, this band is relatively narrow. Within the limits of this band, several maxima occur: 560 nm, 554 nm and 546 nm are the wavelengths of the main ones. It is very curious that this band was not observed in the broadband-luminescence spectrum of the Panasqueira apatites. Neither in the spectrograms of Iwase (1935), nor in the spectrograms of Bachtin (Bachtin & Mashonkin, 1972, p. 62), recorded at 77°K is this band clearly expressed or even visible.

Identical phenomena were observed by the author in apatite crystals from the old tin-tungsten workings at the Greifensteine near Ehrenfriedersdorf in Saxony (Hörning, 1970). In these aggregates, the intensity of this phosphorescence band is such, that the apatite could be photographed in colour in its own light (Plate 4, fig. 2).

The phosphorescence band is of analytical significance. The energy, absorbed during the period of irradiation with blue or ultraviolet radiation, is apparently transferred to groups of ions — 'centres' — which will re-emit part of the energy in the green waveband. The sensitizer-ions in this case are obviously the same as those responsible for the luminescence broadbands: Ce^{3+} and possibly also Eu^{2+}, which can itself act as an activator. The involvement of this ion in the process of phosphorescence is the more probable, as the phosphorescence is localized in the same areas — the clear basal layers — which are showing the characteristic blue luminescence of Eu^{2+}. The green emission is no doubt caused by ions of manganese. It is just possible, that ions of Er^{3+} are involved too, if one is to judge from the wavelengths of the maxima. The same green phosphorescence, by the way, is observed in the willemite from Franklin Furnace: it is caused by Mn^{2+} ions.

We have seen, in the paragraph dealing with broadband luminescence, that Mn^{2+} is also responsible for the strong orange-red luminescence band observed in the green crystals of apatite. The blue-violet crystals with the clear and phosphorescent basal layers do not exhibit this red to yellow luminescence. As a consequence, the complexes of manganese ions, emitting the green phosphorescence, and located in the colourless basal layers, must be of a different nature as those responsible for the orange-red luminescence shown by the green crystals. The ions of manganese must either be of a different valence, or be sited in a different coördination; the symmetry of coördination being lower in the case of the phosphorescent complexes (Bokša & Grum-Gržimajlo 1970, p. 313). It is possible that we are dealing with Mn^{2+} ions, replacing Ca^{2+} ions in sites of different coördination (McConnell, 1973, p. 23). The replacement of calcium ions, sited in the complexes CaO_9 and CaO_6F by Mn^{2+} has been studied with the aid of the EPR-method (Ščerbakova et al., 1970, p. 72 ff).

The question of the orange-red luminescence and the green phosphorescence, both caused by manganese, evidently has not been settled finally. We hope to have demonstrated, however, that the analysis of phosphorescence is of importance as regards the crystalstructure and the presence of ions of trace elements. In the case of the Panasqueira apatites, it has been demonstrated, that ions of manganese are occurring in different sites or valences; ions of Er^{3+} may be present.

Quantitative distribution of trace elements

In the preceding chapters we have reported the following data about the presence of trace elements in the apatites from Panasqueira:

O^{1-}	present in concentrations with definite topological character; concentration highly variable.
Mn^{2+}	ions present in different coördinations, concentration 0.2% by weight.
Mn^{7+}	present in complexes MnO_4^{1-}, replacing the PO_4^{3-} anions; concentration highly variable.

The concentrations of lanthanides, mainly determined in crystal S. 362, are distributed as follows:

Pr^{3+}	11 ppm.	Clarke concentration:	5.5	enrichment:	2	times
Nd^{3+}	110 ppm.	„ „ :	24	„ :	4.6	„
Sm^{3+}	55 ppm.	„ „ :	6.5	„ :	8.4	„
Eu^{2+}	$\leqslant$10 ppm.	„ „ :	1.1			
Eu^{3+}	10 ppm.	The total quantity is enriched		:	>9	„
Tb^{3+}	faint traces.					
Dy^{3+}	25 ppm.	Clarke concentration:	4.5	„ :	5.6	„

The Clarke concentrations of the lanthanide-elements in grams per ton of material from the earth's crust crust were taken from Mason's 'Principles of Geochemistry' (1952).

DISTRIBUTION OF LANTHANIDES; USE OF A STANDARD DISTRIBUTION FOR THE PURPOSE OF COMPARISON OF TYPES OF APATITE

From the assembly of data presented in the previous section, we may conclude that some elements of the lanthanide series are enriched to a higher degree in the Panasqueira apatite, than others. We will now proceed with an analysis of the quantitative distribution of these lanthanides. In the periodical system of the elements, the lanthanides are arranged in a distinctive group (Hubbard, 1969). The chemical properties of the lanthanides are similar, and the lanthanides are therefore never represented as single elements in a mineral: they are always appearing collectively. The element yttrium, although it does not belong to the lanthanides, closely resembles the heavier lanthanide elements in its chemical behaviour, and it always accompanies the lanthanides. When we are speaking of the distribution of lanthanides in minerals, it is customary to include yttrium. The elements are arranged in the series in the order of their atomic number; an exception is made for yttrium, which appears at the end of the series on ground of its chemical properties. The element promethium is usually omitted: it is a radioactive element, and the most stable isotope Pm 145 has a half-life of only about 30 years. For this reason, it never appears in a significant concentration in minerals. The series then comprises the following elements in their order:
La, Ce, Pr, Nd, (Pm), Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y.
The enrichment of lanthanides in minerals is a subject which has received much attention and there is a wealth of publications dealing with the distributions encountered (Gmelin, 1938, contains very many data and references; for the distribution in scheelite see Lagerwey, 1973).

In the next part, under 'quantitative distribution' we will understand the function which relates the concentration of the elements in a certain matrix to their atomic number, with Y at the end of the series. For the sake of briefness, we will employ the letter D with the index a for the distribution in apatite, and reserve the letter C for the distribution of the concentration of the same series of elements (in ppm) in the earth's crust (Clarke). In our case, dealing with the apatites from Panasqueira, we have been able to determine the concentration of relatively few elements of the series. Still, we should like to find means by which it is possible to compare the distribution D_a of an apatite from Panasqueira with a distribution, which can be regarded as a statistical average for all apatites. For this purpose, a procedure was designed, which will be explained in the next section:

The main problems to be solved in order to be able to make a realistic comparison are: primo – the determination of a statistically average distribution of lanthanides in apatite, and secundo – the designing of a method for the adaption of this average distribution which, as we will see, is expressed not in concentration in ppm weight in the mineral, but as a procentual distribution on the total mass of the series of lanthanides, to the fractional distribution D_a, expressed in ppm.

We will first deal with the average statistical distribution. As a basis, it is necessary to collect the largest possible amount of reliable quantative analyses preferably of the full range of lanthanides in apatites of different types of deposit. These data must be collected and treated in a way which is statistically well defined, if not justified. As an example, the genetic types of apatite-bearing deposits should be represented in proportion to their frequency of occurrence. Here we must keep in mind that the composition of the average apatite has to serve as basis of comparison to judge the composition of a certain type. Any type of apatite analyzed must be treated as it were with equal rights when its qualities are compared with the standard. If we intended, for example, to make a statistical analysis of the average weight in men of a certain age and race, living in different nations, then we would never take the weight of a middle-aged man, living in an economically well developed country as a standard of comparison, serving to determine whether the people of some country are underdeveloped or not.

Thus, in our case, it would be wrong to select one specific type of apatite from one deposit as a standard of comparison. Still, such a procedure is actually suggested by some authors: the yellow fluorapatite from the Cerro de Mercado in Mexico has been proposed as a standard; even a detailed chemical formula, comprising the lanthanides, has been designed for it (Young et al., 1969). This apatite has a relatively high concentration of the lighter lanthanides, and it therefore cannot be considered as a fair basis of comparison. Its case is comparable to that of the middle-aged, well to do man in our example.

It is also necessary to consider the published results of analyses critically. If one compares, for example, the results of analyses of different samples obtained with different methods of the one type of apatite from the Cerro de Mercado, published by Young (Young et al., 1969, p. D 86) with those determined by other research-workers for the same material (Brunfelt & Roelandts, 1974), it is evident that the calculated compositions are uncertain. According to Young et al, the concentration of neodymium is, on the average, 1676 ppm ± 294 (standard deviation ± 17.5%); Brunfelt arrives at figures of 1185 ppm ± 9% and 1441 ± 14.5%. A combination of chemical and chromatographical analysis methods would seem to be more reliable (Brunfelt, 1973). One of the grounds of the variable results of analysis is, of course, the great variation in composition of the apatite crystals, even from one deposit. In the Panasqueira deposit, the variations are certainly considerable.

To return to our first problem: in an initial attempt to arrive at an average distribution of lanthanides in apatite, we have used the results of analyses published by Portnov and Gorobets (1969). Their data comprise percentual distributions (by weight) of lanthanides in 22 different types of apatite. From this assembly we have omitted the composition of an apatite from veins of the alpine type in the northern Urals as being extreme, thereby avoiding an obvious distortion of the average. The quantity of apatite from such veins is relatively insignificant anyway. From the remaining 21 compositions, the average percentages by weight of each lanthanide, based on the total mass of the lanthanides were averaged. The resulting percentual distribution is given in the Table 1; the percentual distribution, calculated from the Clarke concentrations, is incorporated:

Table 1. Distribution of lanthanides in apatite, in comparison with the Clarke concentrations.

Light lanthanides (group I) :	La	Ce	Pr	Nd	Sm	Eu	Sum:
Percentage of total mass I + II :	13.02	39.40	7.67	16.91	4.83	0.86	82.69
Percentage of total of Clarke's :	12.14	31.02	3.71	16.18	4.38	0.74	67.17

Heavy lanthanides (group II) :	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sum:
Percentage of total :	2.84	n.d	2.60	0.15	0.97	0.11	0.41	n.d	10.23	17.31
Percentage of total of Clarke's :	4.32	0.61	3.03	0.81	1.69	0.13	1.82	0.54	18.88	31.83

The division in the groups I (light lanthanides) and II (heavy lanthanides) was made for reasons of different chemical and physicochemical behaviour of the elements per group.

If we compare the percentual distribution of the elements in apatite and in the rocks of the earth's crust (Clarke), we see that the distribution of the elements of group I does not differ very much from the Clarke distribution, and shows a selective enrichment of the light elements. The distribution of the elements of group II is significantly different, and shows impoverishment of the heavy lanthanides in apatite. This notable effect is discussed in detail in Gmelin's monography on the rare earths (Gmelin, 1938).

We will now turn to the solution of the second problem, which consists of finding a method of transposition of the percentual distribution, calculated for the 'average apatite', to the series of concentrations, determined for the elements Pr, Nd, Sm, Eu and Dy in the Panasqueira apatite S. 362. From these elements, neodymium is the one, which can be determined with the greatest accuracy by means of its prominent absorption- and luminescencelines; it is also the most abundant element. The neodymium concentration in most apatites is more than sufficient for quantitative analyses; in crystal S. 362 it reaches 110 ppm. From the figures given in Table 1 for the average distribution in apatite, neodymium accounts for 16.91% of the total weight of the lanthanides. If the lanthanide distribution in S. 362 were normal, the total lanthanide content would amount to $\frac{100}{16.91}$ x 110 ppm = 651 ppm, or roughly 0.07% by weight. This is indeed a very low concentration; it is of the same order of magnitude as the lanthanide concentration in the apatites from Ehrenfriedersdorf. The 'normal' concentration of samarium, for example, could be calculated from the 4.83% weight in the average distribution: it would then amount to $\frac{4.83}{100}$ x 651 ppm = 31.5 ppm. The concentration of Sm, determined from the analysis of its specific luminescence (there is a very intense line at a wavelength of 597.50 nm) was 55 ppm. Here, it can be concluded that in respect to neodymium samarium is considerably enriched, by a factor of 1.75 in the Panasqueira apatite. It must be realized, of course, that we have carried out our transposition by the adoption of neodymium as an element of reference. In the same manner, we have calculated concentrations and ratios for the other elements, determined in crystal S. 362:

Praseodymium	trivalent:	11 ppm	determined		
		50 ppm	calculated	ratio	0.22
Neodymium	trivalent:	110 ppm	determined		
		equalized		ratio	1.00
Samarium	trivalent:	55 ppm	determined		
		31.5 ppm	calculated	ratio	1.75
Europium	bivalent:	<10 ppm	estimated		
	trivalent:	10 ppm	determined		
		5.6 ppm	calculated	ratio	>1.79
Dysprosium	trivalent:	25 ppm	determined		
		16.9 ppm	calculated	ratio	1.48

From these figures it can be concluded that the heavier lanthanides are quite considerably enriched in the apatite of Panasqueira, if our average composition is used for the purpose of comparison. The lines of europium are conspicuous in its spectrum, much more so than in other types of apatite with a significant europium content, such as those of St. Goar and Morro Velho.

The typification of apatites, which has been brought forward in the chapter on polarospectrographical analysis, and which resulted in the determination of a few spectral types, might be enhanced by combination with specific distributions of lanthanides in these types of apatite. For this reason, the measurements and calculations, given in this paper for apatite from Panasqueira, were also carried out with representative apatites of three other types: a yellow crystal of apatite from the Cerro de Mercado, a rose-coloured crystal from Fellen-St. Goar, and a yellow monocrystalline fragment of apatite from the formations of talc in the mountainrange of the Grosser Greiner in the Zillertaler Alps in Austria. For the purpose of demonstration of the eventual correlation between the lanthanide distribution and the spectral type, a special sort of graph was constructed, which clearly shows the particularities of distribution expressed as deviations from the standard distribution as defined above.

In Figure 13, the distribution of five lanthanide elements in apatites, representative of four different constitutional types — as defined by their spectral properties —, relative to the neodymium content and the averaged lanthanide distribution (see Table 1) is represented graphically. The medial line represents the level of concentration of neodymium and of the other elements in the 'normal' proportion. The concentration of Nd is indicated in parts per million weight, in arabic numerals. If we are turning now to the apatite from Panasqueira — S. 362 — we see in Figure 13, that the relative concentration for praseodymium is indicated by a line in the appropriate column well below the medial line. We had already calculated the fractional concentration of this element: 0.22 times the 'normal' concentration. The line, indicating the fractional concentration for each element, is located at a distance y (ordinate) from the medial line, calculated from the formula:

$$y = C.{}^{10}\log r$$

C is a scale-constant and r, the ratio of the observed concentration of the element and the concentration of the same element in an average apatite with the same neodymium content.

In S. 362, $r = 0.22$ and ${}^{10}\log 0.22 = -0.6576$, a negative value. As the scale-constant is a positive number, y is negative. When the ratio is greater than one, the logarithm is positive, and y is also positive, indicating relative enrichment. The columns, showing the magnitude of y, are hatched vertically if y is positive: this indicates enrichment. The columns hatched horizontally represent a deficit.

When the distributions of the four apatites represented in Figure 13 are compared, it immediately strikes the eye that the apatite from Panasqueira is a special type: it shows a pronounced excess of concentration of lanthanides with an atomic number greater than 60. Another striking fact is the important deficit of praseodymium, observed in three of the four types of apatite. If we look at the Table 1, we will see that in the 'average' apatite praseodymium is apparently enriched to a remarkable degree: 7.67% of total lanthanide-content in apatite as compared to only 3.71% in rocks. A very high degree of enrichment of praseodymium, according to the data, published by Portnov and Gorobets (1969), appears to be characteristic for apatites from carbonatites, from gabbroid rocks, from alcalic pegmatites, and from some types of metasomatic deposits. The three apatites with a deficit of praseodymium in our graph do not belong to either of these types of deposit, but rather are proper of deposits with a characteristic deficiency of the element in respect to neodymium:

The deposits of the apatite crystals in the formations of iron ore of the Cerro de Mercado in Mexico are supposed to be of pneumatolytic character; originating from volcanic intrusions. The yellow crystals of apatite from Jumilla in the province of Murcia in Spain, belonging to the same group, were formed in volcanic rocks.

The apatites from Panasqueira originate from a granitic magma-intrusion. The deposit is of the pneumatolytic type, modified in a later stage by hydrothermal processes. The tin-tungsten deposits of Saxony are of analogous origin.

The apatites from Fellen-St. Goar were formed on quartz in a high temperature hydrothermal vein.

The yellow apatites, or aspergolites, from the mountain-range of the Grosser Greiner were formed in a talc vein; this deposit is of metasomatic/hydrothermal origin. This type of apatite does not show a deficiency of praseodymium.

A most selective type of enrichment is displayed in the diagram for apatites of constitutional type A: rose-coloured, flat crystals. In these apatites, only neodymium, samarium and europium are appearing in normal concentrations, the concentration of praseodymium and of the heavier elements is very low. From other analyses of apatite from Fellen-St. Goar, it is demonstrated that the cerium content is also low; the strontium concentration, on the other hand, is very high. The magnificent crystals from Morro Velho in the state of Minas Gerais in Brasil are of the same type. The selective incorporation of Nd, Sm and Eu also explains, why the emission lines of europium are so prominent in the luminescence spectrum.

Samarium is usually present in normal concentrations, although there are notable exceptions. Dysprosium concentrations are low, except in the case of the apatites from Panasqueira: Dy has all the characteristics of the heavy lanthanides, but its even atomic number favours its appearance. The other heavy lanthanides are difficult to detect; from experience in crystalgrowing it appears that these ions are not easily accomodated in the lattice of fluorapatite.

The considerations given in this chapter, although of a tentative character, seem to supply good evidence of the existence of a connection between the type of distribution of lanthanides and the spectral type of an apatite, showing char-

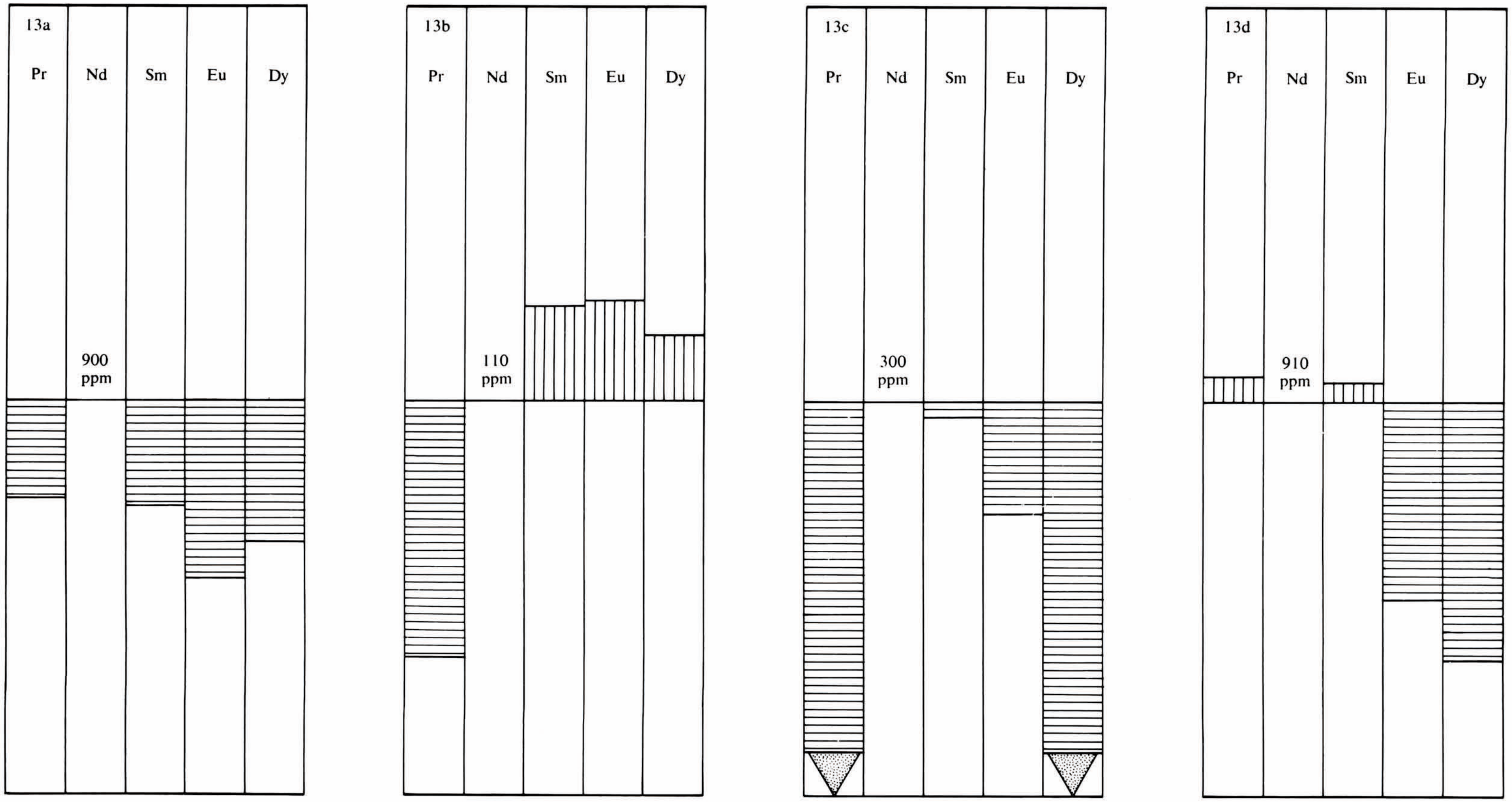

Fig. 13. Enrichment of the trivalent lanthanide ions (Pr, Nd, Sm, Eu, and Dy) in fluorapatites of different genetical types, relative to the Nd^{3+} content, and an averaged distribution for fluorapatites; a: yellow apatite from Cerro de Mercado, sample S. 145, const. type B-2; b: green apatite from Panasqueira, sample S. 362, const. type D-1; c: rose apatite from Fellen-St. Goar, sample S 175, const. type A-1; d: yellow apatite from the Grosser Greiner, sample S 245, const. type C-1.

acteristic substitutions of ions in certain sites of their lattices. The specific configuration of the crystal's electric field in these sites, together with the chemical characteristics of the ions of each lanthanide, seem to be dominant factors which strongly influence the distribution pattern, much more so than ionic radii alone. In order to be able to obtain more data of a higher quality, which are essential for the research into such complex relations of variables, combined programmes of spectrographical and chemical analyses ought to be initiated. Standardized chemical analyses could then supply information about compositions and quantitative distributions, and the spectrographical methods could, apart from supplying additional data of the same nature, yield a wealth of new data on structural details of crystal-lattices. In itself, the idea is not new: similar views have been expressed many times in earlier epochs (Haberlandt, 1938: the author judges the analysis of characteristic luminescence 'very suitable to give an insight in the distribution of trace elements in minerals of different deposits'), but it now seems to be a proper time to follow it up.

Results of optical analyses

As it is desired here to convey to the reader the purport of the experimental work which is presented in this paper in a concise form, we will formulate the motifs and purposes in the first place and thereafter proceed with a presentation of the final results and a discussion of their meaning. The motifs are:

Pleochroism — Optical analysis, description of the phenomena observed in different crystals from the Panasqueira-deposit and explanation of the same. Ions and defects in different areas and loci in the fluorapatite lattice.

Polarized absorption and luminescence spectra — Analysis of information contained in these spectra, observations from broadband spectra and a preliminary investigation of phenomena of phosphorescence. The results are destined for the identification and quantitative determination of ions of trace-elements.

Registration of detailed resolved line structures, observed in absorptions in different ranges of wavelength and caused by trivalent ions of neodymium. The use of line-patterns of wavelength, intensity and characteristics of polarization as informants of specific configurations of the crystalfield in the vicinity of calcium-sites occupied by Nd^{3+} ions. The use of the data for the development of a system of typification.

Correlation of data, obtained in the first and second phases of our research — resulting in a quantitative distribution of lanthanides in the apatite from Panasqueira — and the particular modifications of crystal structure, which can be typified by means of the resolved fine line structures in the neodymium absorptions, observed in the third — preceding — phase. This correlation is effected with the aid of averaged results of quantitative analyses of lanthanides in a whole range of apatites of different origin.

SUMMARY OF OBSERVATIONS AND NUMERICAL RESULTS

Pleochroism — In the various types of apatite-crystals from Panasqueira, two different pleochroic complexes were found to exist: The complex designed 'B' shows up as an intensely blue coloration. The blue colour is caused by a broad maximum of absorption at 720 nm; this absorption is highly polarized in the vectorial orientation $\vec{E} \parallel c$. The complex appears topologically connected to specific areas in the apatite crystals, such as the intersection of (0001) and (11$\bar{2}$0) and planes of growth or contact with crystals of other minerals of the paragenesis. Complexes of identical nature could be observed in crystals of apatite from the tin-tungsten deposits near Ehrenfriedersdorf in Saxony, and from the mines of Sl'ud'anka near Lake Baikal in Siberia. The blue complexes occurring in these crystals are thermally unstable, and could not have been caused by ions of manganese. The complex is thought to consist of groups of O^{1-} centres of electron-deficiency, located in the chains of F^{1-} ions; the specific absorption at 720 nm being a consequence of the interaction between O and F ions. The appearance of 'B' areas which were observed in the interior of flat prismatical crystals from Panasqueira is clearly related to periods of stagnancy in the congruental growth of apatite.

The complex, designed as 'A' is present in concentrations, which vary in different crystals. It causes a yellow-green colour which is conditioned by increased absorption of light in the violet spectral region and by several minor maxima of absorption in the range between 585 nm and 655 nm. The complex is not perceptibly polarized, and it appears to be evenly distributed throughout the entire volume of the crystals. The non-polarized absorption must be ascribed to MnO_4^{1-} ions which are replacing the PO_4^{3-} anions.

The blue colour of some of the apatites from Panasqueira is explained by the predominance of the blue colour 'B' over the yellow colour 'A'. Red-purple and blue-purple colorations, which can be observed in parti-coloured crystals and in some rare homogeneously tinted crystals, must be attributed to Mn^{3+} ions appearing in Ca^{2+} sites.

Polarized absorption and luminescence spectra, broadband luminescence and phosphorescence

The absorption lines which can be observed in various spectral regions between 400 nm and 1000 nm, could be identified by comparison with the spectra of standard preparations of fluorapatite, doped with known concentrations of single lanthanides: they are caused by trivalent ions of neodymium in calciumsites. Polarized spectrophotograms, showing resolved line-structures, were registered in the wavelength ranges between 560 nm and 650 nm and 700 nm and 1000 nm. Although the lines are relatively weak, they are very narrow and well-contrasting. From measurements of absorptivity, the concentration of Nd^{3+} in a representative crystal of apatite was fixed at 110 ppm.

Luminescence lines in the ranges between 560 nm and 650 nm and between 700 nm and 1000 nm could be effectively registered photographically with high resolution and dispersion by the use of a lightsource of excitation, the characteristics of which were adapted to the individual characteristics of excitation of the different ions in the apatite lattice. The lines of Eu^{3+} could be excited with such exclusive selectivity, that lines from other elements were imperceptible. The lanthanides, present in the Panasqueira apatite could be identified with absolute certainty by comparison with luminescence spectra, excited under identical circumstances in standard preparations of fluorapatite doped with single lanthanides in known concentrations. The lines of Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Dy^{3+} could be registered with sufficient intensity for semiquantitative analyses. Traces of Tb^{3+} were observed, but the characteristic lines of the heavier lanthanide elements could not be perceived. The concentrations of lanthanides, measured in crystal S. 362 are: Pr^{3+} : 11 ppm, Nd^{3+} : 110 ppm, Sm^{3+} : 55 ppm, Eu^{3+} : 10 ppm, Dy^{3+} : 25 ppm.

Broadband luminescence was studied by spectrophotometry. The luminescence characteristics of crystals show individual differences. Representative crystals are displaying a luminescence, which appears yellow to the eye. The luminescence-intensity curve of such an apatite shows maxima at wavelengths of 580 nm (orange) and in the violet region between 450 nm and 430 nm. There seems to be another maximum in the ultraviolet region below 400 nm. Some crystals with clear and almost colourless basal layers and a blue or violet bodycolour are displaying a very intense, blue luminescence when excited with shortwave ultraviolet light. The maximum of intensity is occurring between 430 nm and 450 nm. This blue luminescence is characteristic of bivalent ions of europium. The orange luminescence with a peak of intensity at 580 nm is caused by ions of bivalent manganese. Both types of active ions, Mn^{2+} and Eu^{2+}, are radiating energy transferred to them from other ions (sensitizers), such as Ce^{3+} and Eu^{2+}. Different colours of luminescence are perceived by the eye in different crystals from the same deposit. This phenomenon is caused simply by the resultant effect of the two very wide and overlapping luminescence bands, which are showing different relative intensities in different crystals.

From analysis of broadband luminescence it was concluded, that the concentration of Mn^{2+} reaches 0.2% by weight in representative crystals of a lightgreen colour. Eu^{2+} ions appear to be concentrated in crystals of uncommon colour: the concentration is thought to be less than 10 ppm, generally.

Persistent phosphorescence was detected in the uncommon type of blue or violet crystals, notable for their blue Eu^{2+} luminescence. The colour of the phosphorescent light is green; the emission is concentrated in a relatively narrow band, extending from 525 nm to 575 nm. Maxima are situated at 546 nm, 554 nm and 560 nm. The character of thermoluminescent emission is identical. The green emission is supposed to be caused by ions of Mn^{2+} in sites of coördination, different from the sites of Mn^{2+} ions, causing the orange emission, or else by manganese-ions of a different valence. The phenomenon must be further explored, preferably by means of EPR. It is possible that ions of Er^{3+} are also involved. The green phosphorescence is observed in areas of concentration of Eu^{2+}, detected by luminescence. It is highly probable, that these ions act as sensitizers, transferring absorbed energy to the ions of manganese.

Registration of detailed resolved line structures — The registration of absorptions caused by trivalent neodymium-ions was effected in the complex wavebands in the ranges between 560 nm and 650 nm, and between 700 nm and 1000 nm. In the course of systematic registration and analysis of the polarized absorption spectra of about seventy different crystals of apatite from various types of deposit, specific patterns of wavelength, intensity and polarization were discovered. A small number of distinctive spectral types was defined. The phenomenon is caused by peculiarities of the crystalfield in the vicinity of the Nd^{3+} ions, which are replacing

Ca^{2+} ions of different coördinations. An important variable is the mode of compensation of excess spacecharge. The spectrum of the apatite crystals from Panasqueira shows a characteristic structure, typical for the geochemical nature of the deposit. Analogous spectral compositions are observed in the apatites from Ehrenfriedersdorf in Saxony. Evidence is presented in the shape of polarospectrophotograms and diagrams, representing four different types of apatite.

Correlation of data — The apatites from Panasqueira were demonstrated to possess a characteristic structure, which finds its expression in a special type of resolved linestructure of the polarized absorption spectrum of neodymium, as well as showing a specific distribution of lanthanides, notable for the systematic excess of concentration of the heavier lanthanides (atomic numbers exceeding 60). This excess is defined in relation to an average distribution, which was calculated provisionally for apatite as it occurs in geochemically different types of deposit. The same sort of correlation was observed with apatites of other constitutional types, their type of spectral structure being accompanied by a certain type of quantitative distribution of lanthanides. The correlation can be explained by the dominant influence of field configurations, specific for certain types of apatite (also within the group of the fluorapatites), as a primordial variable, together with the chemical characteristics of the lanthanide ions substituting calcium ions. The selectivity of substitution of the calcium ions, resulting in a specific distribution of lanthanides is a dependent variable.

DISCUSSION OF RESULTS OBTAINED; JUSTIFICATION

In the introduction, the spectacular apatite crystals from the tungsten-tin deposits of Panasqueira were indicated as a tempting object of research and very suitable for the evaluation of the effectiveness of original non-destructive methods of optical analysis and of the apparatus which had been developed and constructed for the purpose.

In the course of a detailed account of the experimental work, the discovery of the existence of various types of apatite, which could be distinguished by the fine structure of their absorption-spectra of neodymium, was announced together with the fact that apatites of the same spectral types also exhibited similar exterior distinctive marks.

An assembly of data in relation to ions of trace elements incorporated in the fluorapatite lattice, which were determined by optical methods exclusively, was given in the previous section. Given the complex character of the system of variables involved, these data, however, are only fragmentary and by no means complete or rounded off. Still, they sufficed to reveal the outlines of another relation, in addition to the one mentioned above: it is the relation, which connects the spectral type and the quantitative distribution of the lanthanides. As a result, a logical chain of connections between assemblies of variables appears to be developing; the first three links are: the configuration of the crystalfield, as expressed in the spectral type, the quantitative distribution of the lanthanides, and the exterior distinctive marks. It would seem to be tempting enough to continue the proposed line of research, thereby discovering other links, which could eventually connect to form a closed ring of assemblies of variables. At any rate, the development seems to be promising, and to justify further basic and exploratory research. Here, it is indispensable to coördinate the work and to standardize methods. In this research, the new method proposed could find its place.

The processes of absorption, transfer and radiation of energy, which are determining the phenomena of line and broadband luminescence require special attention. In this sphere, the polarospectrographical method has demonstrated its merits in the shape of the well developed spectrophotograms, a few samples of which are reproduced in the text. Some of these manifestations of processes of energy transfer and radiation, registered photographically, stand in contrast to the effects predicted by conventional theories. An extensive gamma of information on these processes is stored in our spectrophotograms. The photographic registration would seem to be the cheapest, the most objective and the most versatile means of storage of data, in comparison to other methods of registration which are in vogue at present.

The simplicity and cheapness of the proposed method of optical research are certainly assets in periods, when financial means, allotted to the development of fundamental researchwork are ever being reduced — to the detriment of science.

Finally, the complex phenomena of luminescence and phosphorescence caused by ions of manganese in the crystals of apatite from Panasqueira, were demonstrated to be of such a nature so as to make further research promising and attractive.

Summary

The mineral deposits of Panasqueira in the province Beira Baixa in Portugal have yielded a great variety of magnificently crystallized minerals. Of these, accessory apatite crystals are of great scientific interest, because of their well developed crystal forms, colouring, zonal structures, luminescence and many other phenomena. These phenomena are caused by particularities of the crystal lattice. It is our purpose to determine the nature of these particularities, and to relate them to the character of the mineral formation.

The collection of the Rijksmuseum van Geologie en Mineralogie and the author's private collection comprise a number of well developed apatite crystals of varied habit and colouration, which are highly suited to optical investigation. These investigations are conditioned by the necessity to avoid any damage or deterioration of the precious crystals. Thus, only strictly non-destructive optical research methods, such as the polarospectrographical method developed by the author, can be applied.

The results of such an optical investigation are given in this paper; they are demonstrative of the possibilities of the method. A surprising amount of significant information is obtained, concerning the crystal structure of the Panasqueira apatites and the presence of trace elements in them. This information is quite adequate to clearly define objectives and means of an efficient research program.

In the article, the characteristics of the Panasqueira deposits are described briefly, much specialized information being available already in the geological and mineralogical litterature. Resemblances of the apatites from Panasqueira to those from similar deposits, such as the one from Ehrenfriedersdorf in Saxony are discussed. Similarities exist in crystal habit, pleochroic complexes, zoning, and

in the presence of manganese ions of different valences. The difference mainly consists of the presence of a whole range of lanthanide elements with a certain quantitative distribution in the Panasqueira apatite, while the concentration of these elements in the apatites from Ehrenfriedersdorf is exceedingly low.

An assembly of different crystals was selected from the collections mentioned for the present investigation. Particularities of these crystals are accurately described; they are also shown in a number of demonstrative drawings and photographs. The description comprises such features as crystal habit, topologics of growth and colouring, phenomena of redissolution and redepostition, effects of deformation and regeneration and diffusion.

For our study, the following optical methods were employed:
Analysis of the pleochroism, exhibited by the crystals in polarized light.
Analysis of polarized absorption line spectra in the range from 1000 nm to 400 nm, in particular of the fine-structure of the groups of lines, caused by neodymium in the trivalent state.
Analysis of polarized luminescence line spectra in the same wavelength range, employing a special technique for the selective excitation of active ions, in particular those of the lanthanide elements.
Analysis of broadband luminescence, which reveals the presence of maxima caused by some bivalent ions, such as those from manganese and europium.
Effects of phosphorescence were tentatively studied and described. The method, however, still being in the development state, does not as yet allow firm conclusions to be drawn from it.

With the application of these methods, the following results were obtained:
The analysis of pleochroism revealed the existence of two complexes in some of the Panasqueira apatites:
1) A blue complex, strongly polarized parallel to the c-axis of the crystals, thought to be caused by an absorption maximum, centered around 720 nm, originating from O^{1-} sites of electron-deficiencies (holes), located in the F^{1-}-ion-chains. This complex is concentrated in specific zones, preferentially at the intersection of (0001) and $(11\bar{2}0)$, also in pyramidal zones, and to a lesser degree in prismatical zones, in layers. This complex developed during periods of stagnancy of crystal growth.
2) A light yellow-green complex, very weakly polarized, caused by an absorption band, centered around 620 nm, showing several weakly developed maxima. This complex is rather evenly distributed through the entire volume of the crystals. This complex originates from Mn^{7+} in P^{5+} sites, forming tetrahedral complexes MnO_4^{1-}.

In the course of this analysis, parallels are drawn between the Panasqueira apatites and those from Ehrenfriedersdorf, Sl'ud'anka near Lake Baikal and from Templeton, Ontario. Photographs show the effects of pleochroism in crystals from these sites.

The analysis of the absorptionspectrum of the Panasqueira apatite crystals was carried out with the aid of a polarisationspectrograph with a high resolving-power and a high dispersion, constructed by the author. Highly relevant spectrophotograms were obtained, allowing a very detailed analysis of the line spectra. This analysis does not only reveal the nature of the ions, causing the absorption lines, its valences, etc., but it also reveals particularities of the crystal field in the vicinity of the ions.

The absorption lines, observed in the Panasqueira apatites, are caused by trivalent neodymium in calcium sites. They appear in groups in the wavelength-ranges of 806 - 796 nm, 763 - 734 nm, 610 - 565 nm, 532 - 516 nm. Photographs of the absorptionspectra show a multitude of very narrow lines, many of which are strongly polarized.

The intensity determinations of the main lines allowed a global determination of the neodymium content. This was fixed at about 110 ppm, this being a rather low figure for fluorapatites. The Nd content of the apatites from Ehrenfriedersdorf is so low as to render the element virtually undetectable by absorption.

The structure of the main group of Nd-lines between 592.50 and 568.00 nm was observed in detail and represented diagrammatically, showing wavelengths, intensities, and polarisation. This diagram is placed in opposition to diagrams, taken from the Nd spectra of other types of apatite, like those from Fellen-St. Goar (FRG), from the Cerro de Mercado (Mexico), and from the Greiner Mountain (Austria).

In the course of his extensive studies of the absorption spectra of Nd^{3+}, generally observable in apatites, the author has been able to classify the apatites by their spectra in a reduced number of types. The crystal-field patterns of these apatites in the vicinity of the Nd^{3+} ions are characteristic and very similar in each of these types. The diagrams, given for four different types, show the differences very clearly. It was found that the Panasqueira apatite is of a type, distinct from the representatives of the other types mentioned. The apatites from Ehrenfriedersdorf are of the same type.

Using special methods for selective excitation of luminescence, the luminescence lines of active ions of lanthanide-elements present could be enregistered. Several spectrophotograms are shown in the text; they demonstrate the polarisation effects very clearly. The lines appearing in the polarized luminescence spectra could be determined with certainty as belonging to specified lanthanides by direct comparison with the spectra of samples of synthetic fluorapatites doped with known concentrations of specific lanthanides. Sample spectra of Eu^{3+} fluorapatite are shown; they are demonstrating the effects of selective excitation. In the wavelength-range from 400 nm to 1000 nm, the lines of Pr^{3+}, Nd^{3+} (confirming the absorption-analysis), Sm^{3+}, Eu^{3+} and Dy^{3+} are present with intensities, allowing a reasonable estimation of the concentration. Trivalent terbium may be present in traces. In addition to the 110 ppm Nd, 11 ppm of Pr^{3+} was determined, 55 ppm of Sm^{3+}, 10 ppm of Eu^{3+} and 25 ppm of Dy^{3+}. Effects of energytransfer, influencing intensities, were taken into account.

Broadband luminescence-analysis of the apatite crystals was carried out with the aid of a spectrometer in the visible light range. The analysis shows the presence of a strong maximum at about 580 nm, and of others at 450 - 430 nm and a shorter wavelength. The maximum at 580 nm is caused by Mn^{2+} ions, radiating energy transferred from other ions, absorbing in the ultraviolet range. The concentration of the bivalent manganese was estimated to be about 0.2% by weight. The maximum at 450-430 nm is probably caused by Eu^{2+}. This intense blue luminescence can be observed to be localized in layers, adjacent to the end faces (0001). In these layers the Mn^{2+} luminescence is not observed. The concentration of Eu^{2+} is estimated at 10 ppm or less, locally.

Finally, experiments were conducted with crystals of a particular habit, in which phosphorescence could be induced by exposition to pulses of light from a xenon flashdischarge tube. The phosphorescent complexes are concentrated in clear basal layers of crystals, showing a blue or violet bodycolour. Eu^{2+} luminescence is concentrated in the same location.

Halflife periods of one minute and a visibility during 15 minutes or more are typical. The phosphorescent emission is concentrated in a rather narrow band between 525 nm and 575 nm; several maxima can be observed. It appears that irradiated energy is absorbed by sensitizers like Ce^{3+} and Eu^{2+}, and reradiated by Mn^{2+} ions. The coördination-pattern of the Ca^{2+} site, occupied by the Mn^{2+} ions, determines the character of the phosphorescence. It is possible that Er^{3+} ions are also involved.

However, the results mentioned are of a tentative character, the method still being in a stage of development. Results are published in the hope of stimulating research on the behaviour of Mn^{2+} ions in apatite.

The quantitative distribution of elements of the lanthanide group in representative crystals from Panasqueira was studied on the basis of data, obtained by analysis of absorption and luminescence. A standard quantitative distribution was tentatively calculated to represent a 'normal average' fluorapatite from data, provided by Portnov and Gorobets (1969) about the composition of a number of apatites from various types of deposit. This distribution, calculated for the purpose of comparison, clearly shows the tendency for preferential enrichment of the lighter lanthanides. Comparison of the distribution of Pr, Nd, Sm, Eu, and Dy in the apatite from Panasqueira and in the 'normal average' apatite shows a pronounced preferential enrichment of the heavier lanthanides: Sm, Eu and Dy are appearing in concentrations, higher than normal. The concentration of Eu, in particular, is notable. Similar lanthanide distributions were calculated for three other types of apatite, distinguishable by their typical neodymium line-absorptions and by their external distinguishing marks.

The work, presented in this paper, resulted in the determination of three assemblies of data (exterior marks - particularities of the crystalfield - lanthanide distribution), which form a complex, judged to be characteristic for all apatites belonging to one group. A great advantage of the method proposed is the relative ease with which the spectral type of an apatite can be defined by its neodymium spectrum.

It is hoped, that the result of the present study on the properties of the apatites from the Panasqueira deposit will be judged as being representative of the possibilities, proper of the new method and apparatus, and that it may lead to further development and a wider application.

References

Transliteration of Russian to Roman according to official table published by the Academy of Sciences, Moscow, USSR.

Bachtin, A. I. & V. I. Mashonkin, 1972. Luminescence of apatites. — Communication V 144: 60-66 (in Russian).

Bachtin, A. I., N. M. Nizamutdinov & V. M. Vinokurov, 1972. Optical absorptionspectra and colour of apatites. — Izv. Akad. Nauk, Geol. Otdel., 1972, 12: 102-108 (in Russian).

Blasse, G. & A. Bril, 1970. Characteristic luminescence. — Philips Techn. Rev., 31, 10: 304-334.

Bokša, O. N. & S. V. Grum-Gržimajlo, 1970. About the determination of the valence and the coordination of the ion Mn in crystals by means of optical spectra. In: Spectrography of Crystals. — Izdat. 'Nauka', Moscow: 313-320 (in Russian).

Bril, A., G. Blasse, A. H. Gomes de Mesquita & J. A. de Poorter, 1971. Snelle phosphoren. — Philips Techn. Tijdschr., 32, 5: 125-131.

Brunfelt, A. O., 1973. Separation of Rare Earth Elements from Apatite. — Separation Sci., 8, 5: 623-625.

Brunfelt, A. O. & I. Roelandts, 1974. Determination of Rare Earths and Thorium in Apatites by Thermal and Epithermal Neutron-activation Analysis. — Talanta, 21: 513-521.

Cardoso d'Orey, F., 1967. Tungsten-tin mineralization and paragenesis in the Panasqueira and Vale da Ermida mining districts, Portugal. — Comun. Serv. Geol. Portugal, 52: 117-167.

Foshag, W. F., 1923. Mineralogy and Geology of Cerro Mercado, Durango, Mexico. — Proc. U.S. Natl. Mus., 74, 23 (2768): 1-27

Gaines, R. V. & D. Thadeu, 1971. The Minerals of Panasqueira, Portugal. — Mineral. Rec., 2, 1: 73-78.

Gmelin, L., 1938. Handbuch der Anorganischen Chemie: Seltene Erden. TeilA - Lieferung 1. System-nummer 39. — Verlag Chemie GmbH, Weinheim.

Grisafe, D. A. & F. A. Hummel, 1970. Crystal chemistry and Color in Apatites, containing Cobalt, Nickel, and Rare-Earth Ions. — Amer. Mineral., 55: 1131-1145.

Haberlandt, H., 1938. Spektralanalytische Untersuchungen und Lumineszenzbeobachtungen an Fluoriten und Apatiten. — Sitzungsber. Akad. Wiss. Wien, Math.-naturw. Kl., Abt. IIa, 147, 3-4: 137-150.

Harber, P. R., E. I. Nikitina, V. I. Sotnikov & M. J. Ščerbakova, 1970. New data about the character of luminescence and the paramagnetic properties of the ions of manganese in accessory apatite. In: V. M. Kljarovski (ed.): Research of structural details of minerals with modern physical and chemical methods. — Izdat. 'Nauka', Sibirsk. Otdel., Novosibirsk: 95-103 (in Russian).

Hörning, W., 1970. Greifensteingebiet, Thum, Ehrenfriedersdorf, Geyer. — Brockhaus Wanderheft, 132.

Hubbard, H. D., 1969. Key to the Periodic Chart of the Atoms. — Sargent-Welch Sci. Cy., Skokie, Ill.

Iwase, E. I., 1935. Über das Fluoreszenzspektrum des Apatites im Ultravioletten Lichte. — Sci. Papers Inst. Phys. Chem. Research, Japan, 27, 567-571: 1-8.

Köhler, A. & H. Haberlandt, 1935. Lumineszenzanalyse von Apatit, Pyromorphit und einige anderen Phosphaten. — Chemie der Erde, 9 (1934-1935): 88-99.

Lagerwey, A. A. F., 1973. Une nouvelle méthode polarospectrographique, appliquée aux recherches typochimiques des minéraux. — Thesis State Univ. Utrecht, Grafisch Bedrijf Schotanus & Jens B.V., Utrecht.

——, 1974a. A practical method for optical spectroscopy of crystals. — Geologie Mijnbouw, 53, 2: 51-64.

——, 1974b. Detection of structural varieties of red gem spinels from Ratnapura, Sabaragamuwa province of Sri Lanka. — Scripta Geol., 27: 1-27.

McConnell, D., 1973. Apatite, Its Crystal Chemistry, Mineralogy, Utilization, and Geologic and Biologic Occurrences. — Springer Verlag, Wien & New York.

Mason, B., 1952. Principles of Geochemistry. — J. Wiley & Sons, New York.

Portnov, A. M. & B. S. Gorobets, 1969. Luminescence of apatite from different rock types. — Dokladi Akad. Nauk SSSR, 184: 199-201 (in Russian).

Royal Horticultural Society, 1975. R. H. S. Colour Chart, with table of crossreferences. — Royal Horticult. Soc., London.

Ščerbakova, M. J., A. A. Godovikov, L. G. Gilinskaja, L. G. & Z. V. Vasil'eva, 1970. Research on apatites of different genesis by means of the electron paramagnetic resonance method. In: V. M. Kljarovski (ed.): Research of structural details of minerals with modern physical and chemical methods. — Izdat, 'Nauka', Sibirsk. Otdel., Novosibirsk: 71-94 (in Russian).

Young, E. J., A. T. Myers, E. L. Munson & N. M. Conklin, 1969. Mineralogy and geochemistry of Fluorapatite from Cerro de Mercado, Durango, Mexico. — U.S. Geol. Survey Prof. Paper 650 D: 84-93.

Manuscript received 15 January 1977.

Plate 1

Fig. 1: Twinned crystal groups of similar habit from Panasqueira (S. 406) and from Ehrenfriedersdorf (S. 388; on the right). The photograph, taken in polarized light, shows areas of blue pleochroic colour.

Fig. 2. Aggregate consisting of blue-gray, lenticular apatite crystals covered with muscovite, sample S 363 from Panasqueira.

Plate 2

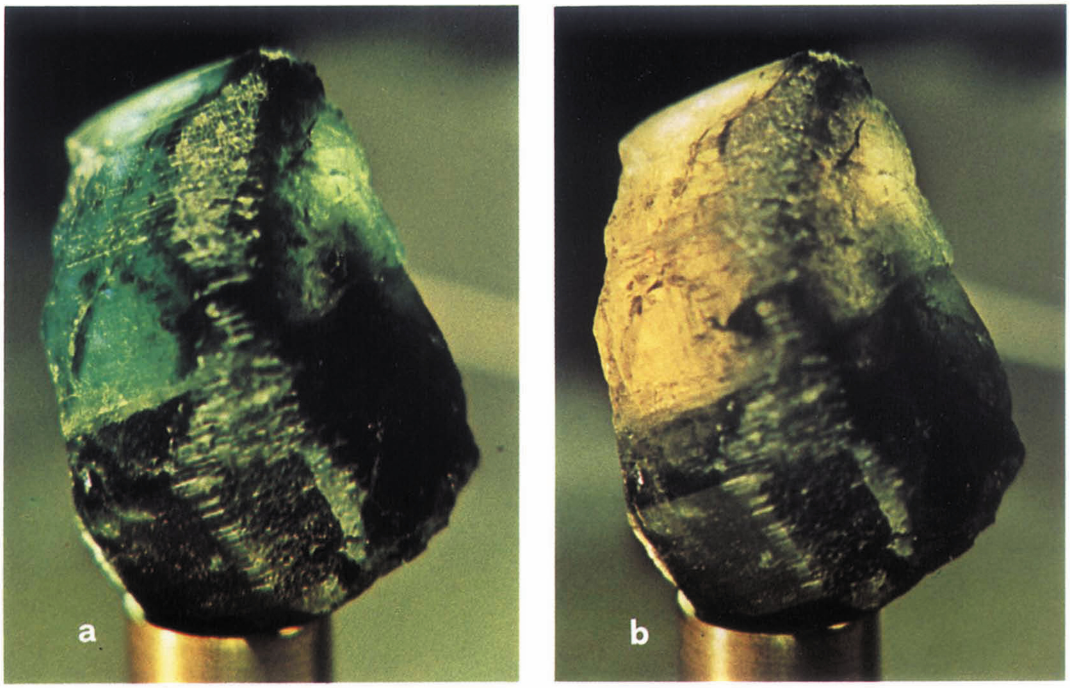

Fig. 1. Green monocrystal of apatite from Panasqueira (S. 248); a: light polarized parallel with the c-axis; b: light polarized perpendicular to the c-axis.

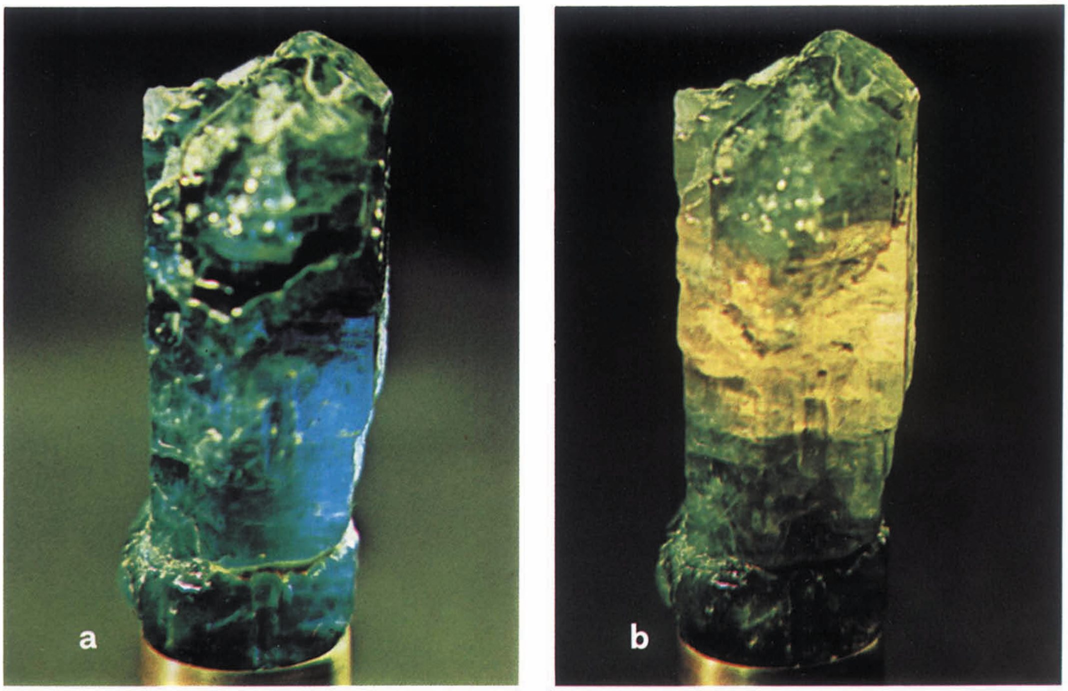

Fig. 2. Moroxite crystal from Sl'ud'anka, near Lake Baikal; a: light polarized parallel with the c-axis; b: light polarized perpendicular to the c-axis.

Plate 3

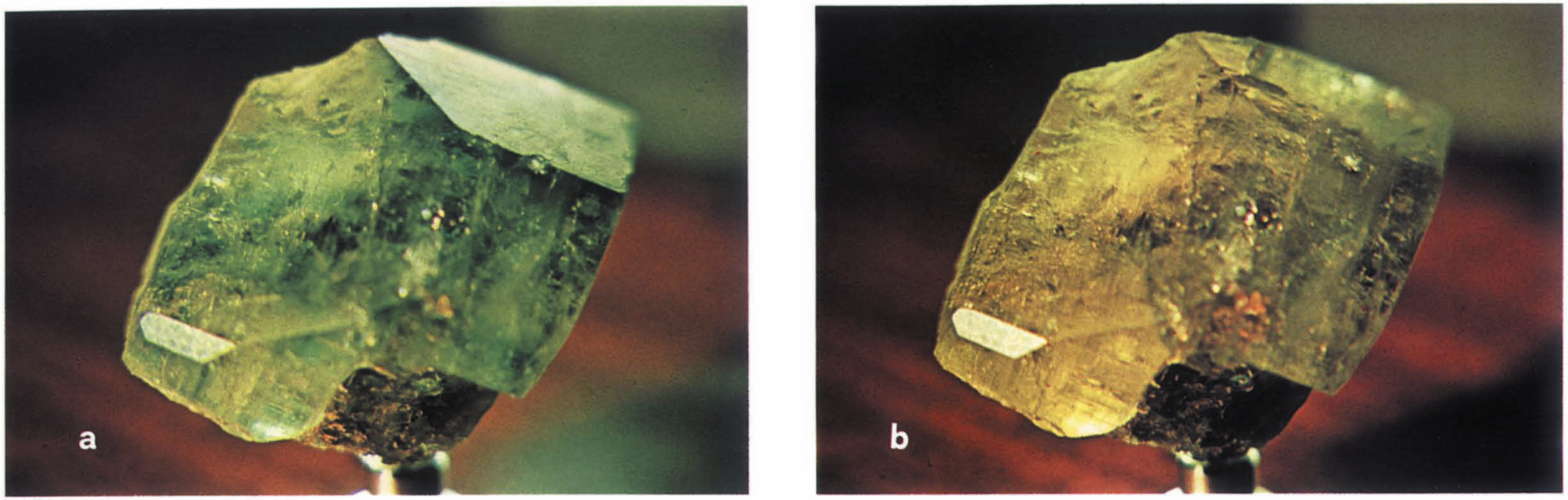

Fig. 1. Crystal S. 362 from Panasqueira; a: light polarized parallel with the c-axis; b: light polarized perpendicular to the c-axis.

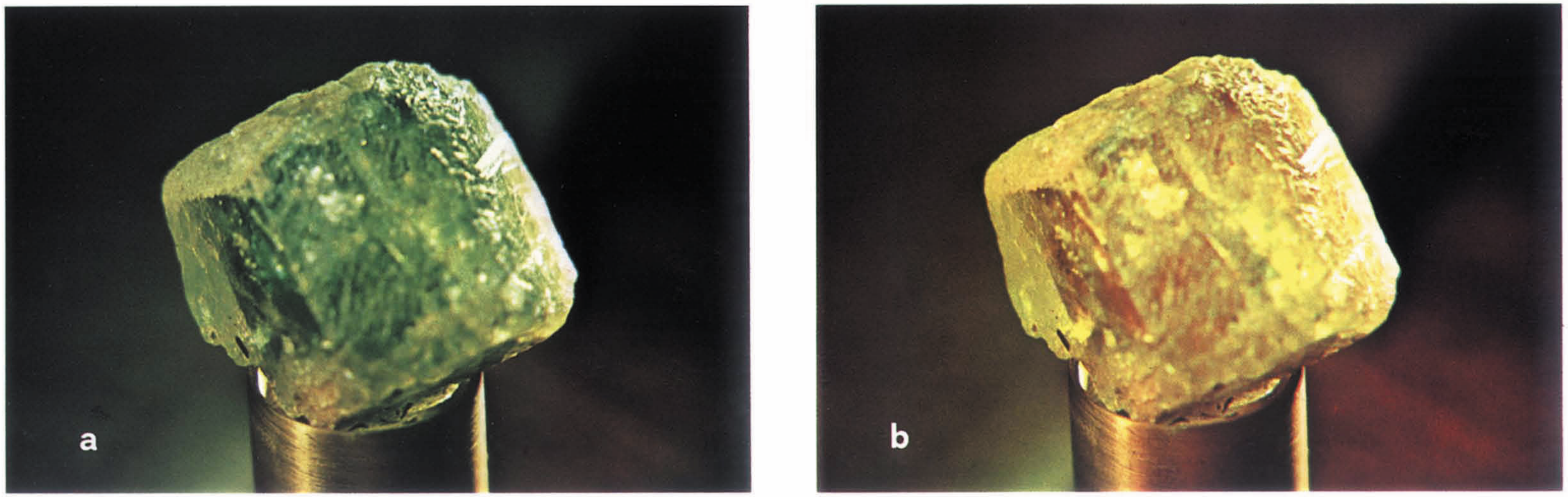

Fig. 2. Green apatite crystal from Templeton (Ontario, Canada); a: light polarized parallel with the c-axis; b: light polarized perpendicular to the c-axis.

Plate 4

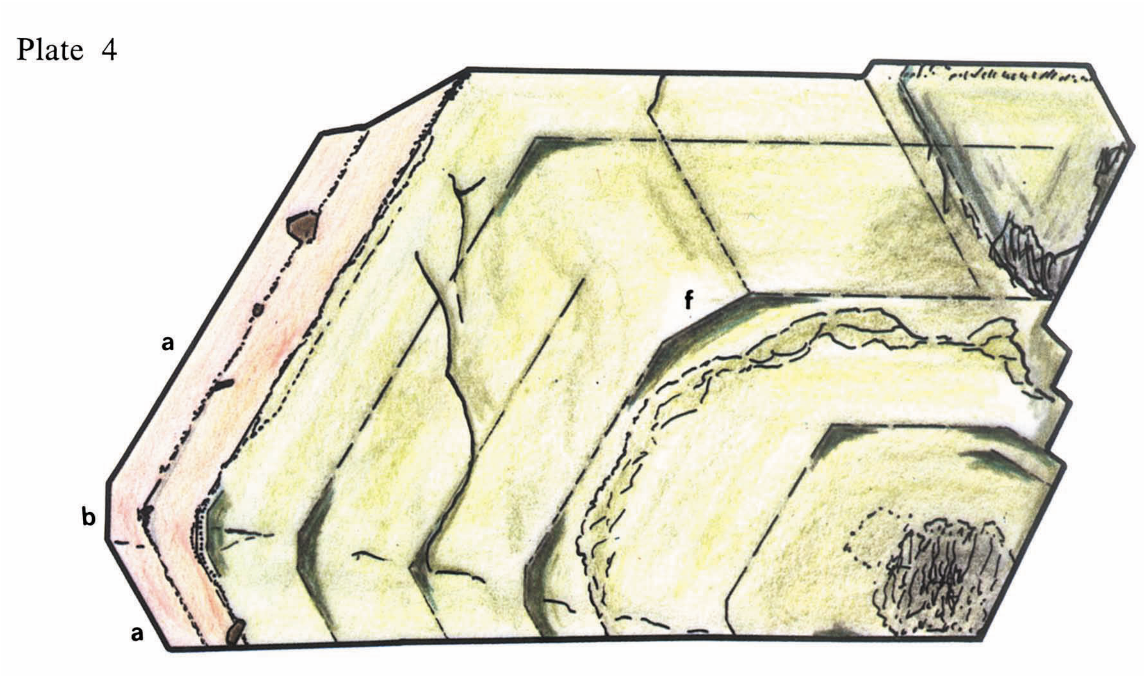

Fig. 1. Drawing of a flat prismatic apatite crystal from Panasqueira (S. 409) showing zoning caused by discontinuities in growth, and diffused zones of the pleochroic complex 'B' formed during periods of stagnancy of growth. The top is a perfectly flat termination c. Crystal faces a=$(10\bar{1}0)$, b=$(11\bar{2}0)$, c=(0001); f=zone of diffused blue colour at b $\nparallel$ c, $\vec{E}$ // c.

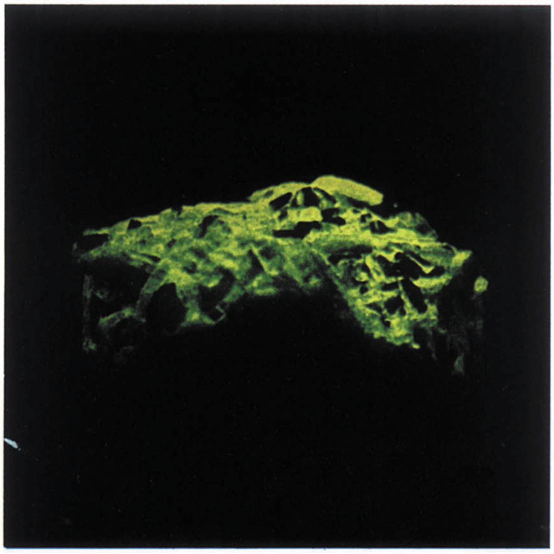

Fig. 2. Group of apatite crystals from the Greifensteine near Ehrenfriedersdorf (G.D.R.) photographed in their own phosphorescent light.