

Further investigations into the nature of the materials chlorophaeite and palagonite

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SUMMARY. Specimens of chlorophaeite and palagonite obtained from eight countries were examined using a variety of techniques. Investigations showed the materials to be not simple substances but multiphase composites. The confusion that existed in the literature necessitated a revision of the nomenclature and construction of criteria for identifying the two materials. Their nomenclature has been expanded: chlorophaeite to include the following phases; phase I, green and isotropic; phase II, golden yellow and isotropic; phase III, darker than phase II and anisotropic; a fourth phase, named associated material (A), microcrystalline, pale green and sometimes pleochroic. Similarly for palagonite, a golden yellow glassy phase, essentially basaltic glass (no new name needed); phase X, a hydrated phase slightly darker in colour than the glassy phase, also isotropic; phase Y, dark brown to orange, microcrystalline, anisotropic, found adjacent to phase X; associated material (M) green, anisotropic, often chlorite or chloritic. Both of the above descriptions were based on neotypes, established during the work. X-ray diffraction data for the two materials are given together with microprobe analyses of some of the phases of the two materials.

THE name chlorophaeite was first used by MacCulloch (1819) to describe a 'mineral' that exhibited a striking colour change from green to brown on exposure to the atmosphere. Nearly one hundred and fifty years later this name is still used; around it, however, has been built much controversy. The intention of the research was to obtain as much information as possible on the material. Frequently when the term chlorophaeite is encountered in literature concerning basalts, it is associated with the name palagonite. This name was first used by Von Walterhausen (1845) to describe material in the groundmass of some Sicilian tuffs. Palagonite, like chlorophaeite, is a name that has suffered much from ambiguity.

Chlorophaeite is known to occur in many of the basalts, dolerites, and tholeiites of the Midland Valley of Scotland. These rocks are quarried extensively for use as aggregate in concrete and as roadstone. Brady (1933) suggested that the presence of chlorophaeite within such aggregates may be responsible for, or contribute to, the abnormal properties exhibited by some aggregates. It is these properties that give rise to deleterious effects in concrete mixes into which they are incorporated. Thus further information on chlorophaeite might well prove of value in understanding its role in concrete failure.

Materials investigated. Specimens were obtained from America, Australia, the Canary Islands, Iceland, India, Ireland, Scotland, and the U.S.S.R. Some specimens used were from the Building Research Station collection, all specimens were given a Building Research Station collection number (BRS No.) and are listed in table I. The

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As a result of examination of several specimens of material alleged to be chlorophaeite and palagonite and comparison of these specimens with two specimens

TABLE I. *Specimens investigated*

No.	BRS No.	Original description	I*
1†	P. 1179	Basalt with chlorophaeite, Co. Antrim, Ireland	C
2	P. 935/3	Olivine dolerite, Parkthorn, Troon, Scotland	N
3	P. 857/C	Olivine dolerite, Hillhouse, Troon, Scotland	N
4	P. 857/D	Olivine tholeiite, Kaimes, Edinburgh, Scotland	C
5	P. 857/E	Teschenite, Craigie Hill, Midlothian, Scotland	N
6	P. 857/K	Olivine basalt, Burnside, Angus, Scotland	N
7	P. 1233	Palagonite, Ardtun, Mull, Scotland	P
8	P. 1234	Basalt, Deccan Traps, India	N
9	P. 1235	Dolerite, Canary Islands	N
10	P. 1244/5	Dolerite, Grande Ronde, Oregon, U.S.A.	C
11	P. 1244/6		C
12	P. 1244/11	Basalt, Urals, U.S.S.R.	C
13	P. 1244/12	Tholeiite, Kaimes Quarry, Edinburgh, Scotland	C
14	P. 1244/13	Tholeiite, Dalmahoy Hill, Edinburgh, Scotland	C
15	P. 1244/14	Tholeiite, N. Side, Dalmahoy Hill, Edinburgh, Scotland	C
16	P. 1259/4	Icelandic basalt with chlorophaeite	C
17	P. 1259/10		C
18	P. 1259/10	Chlorophaeite extracted from 17	C
19†	P. 1259/14	Palagonite tuff with zeolites, Iceland	P
20	P. 1259/15	Palagonite tuff, Iceland	P
21	P. 1259/16		P
22	P. 1259/17	Craignurite	N

* 'I' refers to the identification of material, as a result of the investigation. 'C' indicates the presence of chlorophaeite; 'P' the presence of palagonite; 'N' that neither chlorophaeite nor palagonite are present.

† Neotype specimen.

selected as neotypes of chlorophaeite and palagonite, it was concluded that the two materials were different. The neotypes (P1179 and P1259/14, table I) were selected as being those specimens most nearly approaching the descriptions of the type materials, and are deposited at the Building Research Station. Chlorophaeite and palagonite were thought to be two distinct materials as they exhibited differences in internal structure and external morphology, chemical composition, mode of occurrence, and colour.

Methods of distinction and expanded nomenclature. Evidence for the difference in structure was obtained from X-ray diffraction. A Guinier focusing camera and a Philips powder camera were used and the results are shown in table II. The most

obvious difference between the chlorophaeite and palagonite patterns is that the palagonite pattern contains far more lines than the chlorophaeite pattern.

Closer examination of the chlorophaeite patterns shows that there are certain lines common to the majority of specimens, at 4.6, 4.0, 3.15, 3.0, 2.54, and 1.55 Å. Three specimens also exhibited a line at 15.0 Å; taking this line into consideration these patterns appeared similar to those of montmorillonite, saponite, and nontronite. This 15 Å line is not common to the majority of specimens, and cannot be taken as characteristic.

The palagonite patterns also show a series of lines common to the majority of palagonite samples. These lines have the spacings 4.8, 4.07, 3.74, 3.45, 3.02, 2.85, 2.65, 2.54, 1.55 Å. Again three samples exhibit a line at 15 Å, but not in the majority of specimens. There are a few lines that appear to be common to both chlorophaeite and palagonite and some of these lines correspond to those of montmorillonite, beidellite, griffithite, and nontronite; these are, however, insufficient to afford a positive identification.

Different patterns were obtained from one specimen of chlorophaeite; while accepting the possibility of contamination this could also be due to variation in the crystallinity of the material. As it all came from the same specimen it suggests that the material is inhomogeneous, which is verified by optical examination (see later). The same applied to palagonite.

The greater number of lines exhibited by palagonite suggests that one or more phases exhibit a greater crystallinity than the chlorophaeite phases. The majority of the material examined comprises a mixture of phases, and the patterns are predominantly similar to those of a microcrystalline material.

The electron probe microanalyser showed that chlorophaeite and palagonite differed chemically, both quantitatively and qualitatively. The two neotype specimens (P1179 and P1259/14) were examined on the electron probe to see if any difference existed between the chemical compositions of the two specimens, to establish the elemental distribution within each of the two specimens, and to determine any variation in elemental distribution between specimens. The results are shown in table III and fig. 8.

It can be seen from analyses 2 and 3 that corresponding phases (see later) of chlorophaeite and palagonite vary considerably in composition; the SiO₂, Al₂O₃, MgO, and CaO percentages are noticeably different. The element distribution micrographs (fig. 8) show that the distribution of the same element within corresponding phases of chlorophaeite and palagonite is different for the three main elements other than silicon.

Optical microscopy of each of the two specimens revealed several phases. Thus when comparing element distribution micrographs, care must be taken to compare only those phases in both specimens that can in any way be called equivalent. It will be shown later that some similarities do exist between phases in different specimens. The distribution micrographs of palagonite and chlorophaeite are marked to show two regions A, B, and II, III respectively, fig. 8. The two regions to compare are B and II. The area B is seen to be magnesium- and aluminium-rich and iron-poor. The

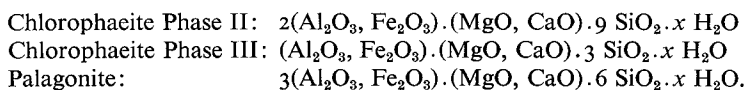
area II can be seen to be magnesium- and aluminium-poor and iron-rich. The silicon distribution pictures were not included as the distribution was seen to be uniform throughout. Thus the neotype specimens could be seen to differ chemically, both quantitatively and qualitatively.

TABLE III. *Analyses of chlorophaeite and palagonite neotype specimens P1179 and P1259/14, using the electron probe (these are point analyses)*

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Total
Palagonite parent glass	46.7	4.7	7.2	23.2	0.40	7.7	10.3	100.2
	46.3	4.8	7.0	24.1	—	8.2	9.7	100.1
	51.5	3.2	9.1	18.8	—	7.9	9.4	99.9
Palagonite phase X*	44.4	0.29	28.9	10.6	0.38	9.6	5.8	99.97
Chlorophaeite phase II	59.9	0.33	5.2	29.4	0.40	3.6	1.4	100.23
	52.1	0.34	3.9	36.5	—	5.2	2.1	100.14
Chlorophaeite phase III	51.0	0.32	5.7	30.3	0.27	10.4	2.0	99.99
	43.1	0.5	5.8	38.8	—	7.9	3.9	100.0

* Values estimated from element distribution profiles.

The chemical composition of the palagonite and two chlorophaeite phases can be roughly represented by the formulae below, which show only the relative proportions of the major oxides:

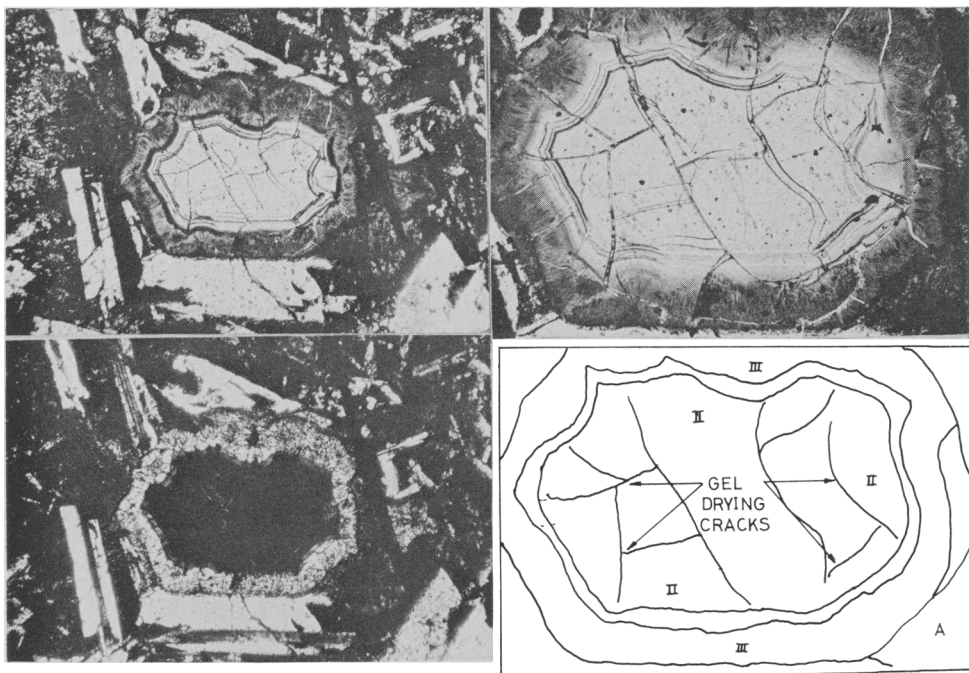


Optical microscopy was used to detect differences between the optical properties and microstructure of the two materials. The host rocks containing the neotype specimens were examined in thin section; photomicrographs of the two neotype specimens are given, figs. 3 and 5, together with diagrammatic explanations of them. Many specimens (as listed) were also examined and as a result of these examinations the following conclusions were drawn:

The materials chlorophaeite and palagonite are not simple substances, but multi-phase composites; thus when the name chlorophaeite or palagonite is used, it must be expanded to indicate which phase or phases of the material are thought to be present. Some of the material previously described as chlorophaeite is not chlorophaeite; material previously identified as chlorophaeite in some Scottish rocks has been identified as chlorite, serpentine, iddingsite, and microcrystalline material chloritic in nature.

Examination of the neotype specimen of *chlorophaeite* revealed that in regions generally referred to or described as chlorophaeite several phases were present: A totally isotropic phase, green in colour, which is gel like and shows gel drying cracks; this green phase is extremely rare; suggested name, phase I. A totally isotropic phase, yellow-orange to brown in colour, which is also gel like and shows gel drying cracks;

this phase is more common than the first; suggested name, phase II. A birefringent, microcrystalline phase, which is often very slightly darker in colour than phase II; this phase is thought to be a more crystalline form of the second phase. Both colour and form of crystallinity are seen to vary in this phase; suggested name, phase III. And a birefringent chloritic phase green in colour and sometimes pleochroic. The relationship of this phase to the third is uncertain. It could represent a further



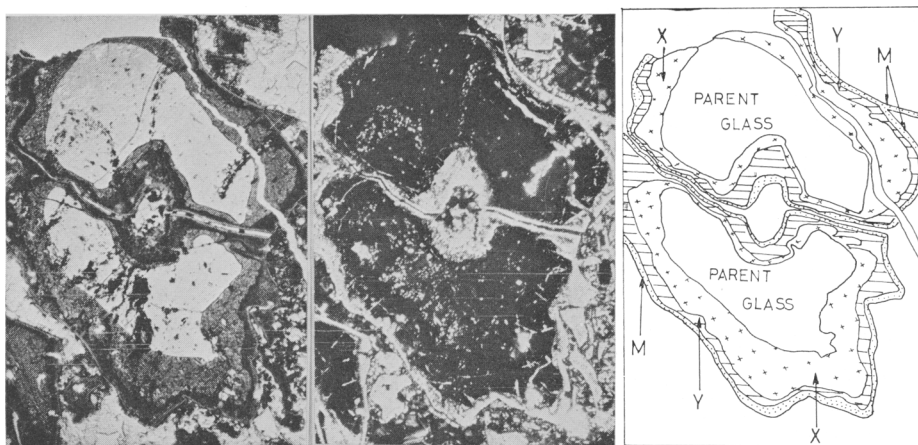
FIGS. 1-4: Fig. 1 (top left) neotype material of chlorophaeite in basalt ($\times 37.5$; plane polarized light). Fig. 2 (bottom left) as fig. 1 but under crossed nicols. Fig. 3 (top right) neotype material of chlorophaeite, higher magnification to show structure ($\times 77.5$; plane polarized light). Fig. 4 (bottom right) diagrammatic sketch to show phases II, III, and associated material (A).

crystallized form of the third phase, or it could represent a decomposition product of the third phase.¹ Colour and form of crystallinity are seen to vary in this phase; suggested name, associated material A.

Similarly, examination of the neotype specimen of *palagonite* revealed that in regions generally referred to or described as palagonite the following phases were present: An inner glassy phase pale-yellow to orange in colour, and totally isotropic. This phase is often seen to contain microlites of olivine, pyroxene, and plagioclase feldspar (all fresh); no new name required as this is basaltic glass. A golden yellow

¹ This expanded nomenclature for chlorophaeite is different to that previously proposed by the author, Stokes (1968). It is intended that the previous nomenclature be abandoned in preference to that described above, the reason being that the earlier nomenclature used symbols that are commonly associated with phases exhibiting a thermal relationship. The same applies to the renaming of palagonite.

isotropic phase, noticeably darker than the first phase, with which it lies in contact, the boundary being sharp. Microlites are also present, but show signs of alteration; suggested name, phase X. A birefringent, microcrystalline phase, slightly darker in colour than the previous phase of which it is thought to be a crystalline form. The colour and form of this phase are seen to vary; suggested name, phase Y. And a crystalline birefringent phase chloritic in appearance. The relationship of this phase to the previous phase is uncertain. It could be a more crystalline form of the



Figs. 5-7: Fig. 5 (left) neotype material of palagonite ($\times 37.5$; plane polarized light). Fig. 6 (centre) as fig. 5 but under crossed nicols. Fig. 7 (right) diagrammatic sketch of fig. 5 showing the parent glass, palagonite phases X and Y, and associated material (M).

previous phase or a decomposition product of it. The colour and form of this phase are seen to vary; suggested name, associated material M.

In both the chlorophaeite and palagonite specimens variation was observed in the nature of the material constituting phase III, associated material (A), phase Y and associated material (M). The variation is mainly in form and colour of the crystalline material. The optical properties of these two materials were for the most part indeterminate. Refractive index measurements were made on samples of Icelandic palagonite, mainly phase X, and Icelandic chlorophaeite (phase II) and the values were: 1.49-1.50 and 1.56-1.57 respectively. While it is appreciated that refractive index varies with water content in such substances, and that the water content is variable, these values seemed sufficiently different to justify inclusion.

Examination of many thin sections revealed that chlorophaeite and palagonite tended to be associated with different minerals: Palagonite was commonly found associated with zeolites and chlorophaeite was not.

Electron microscopy of specimens 1, 7, 8, 10, 12, 16, 19-21 revealed differences in the microstructure of the two materials. The interpretation of electron micrographs is at the best of times subjective and bearing this in mind the following conclusions were drawn:

Palagonite specimens under the electron microscope showed fragments of glassy material exhibiting conchoidal fracture, whereas chlorophaeite specimens did not. It is believed that distinction can be made between the different phases of chlorophaeite (excluding phase I). Similarly for palagonite the parent basaltic glass was visible, exhibiting conchoidal fracture and this could be distinguished from more crystalline material, which was taken to be the X or Y phase or both. The distinction between chlorophaeite (phase II) and the remaining chlorophaeite phases is one of crystallinity. Phase II and the palagonite parent glass are less crystalline than phase III and material (A), and phase Y and material (M), respectively. The increase in crystallinity is shown by the material appearing to be more platy in form, suggesting a more definite organization of internal structure compared with the amorphous appearance of phase X and the conchoidally fractured parent glass.

Some material alleged to be chlorophaeite, when examined under the electron microscope, bears no resemblance to the neotype material of chlorophaeite, but resembles electron micrographs of montmorillonite in the literature, e.g. Bates (1952).

Criteria for identification of chlorophaeite and palagonite. The confusion between chlorophaeite and palagonite has led the author to propose a series of criteria to be used when attempting an identification of either of these two materials. The easiest form of examination of such material is petrological. Thus, optical criteria may first be used, and if doubt exists after this, then chemical, X-ray, and electron microscopic criteria should be called upon.

Conditions that must be fulfilled when making an optical identification of material thought to be either chlorophaeite to palagonite are suggested: Positive identification of chlorophaeite can be made if the material being examined contains material resembling phases I, II, and III, or if it contains material resembling phases II and III. The presence of material resembling phase III only raises a problem. Phase III corresponds approximately to a crystalline form of phase II. Thus, if crystallization has been complete then phases I and II will no longer be present; this means that the origin of phase III material in such cases cannot be definitely linked with phases I and II. Until a characterization of phase III has been performed, the author feels reluctant to base an identification of chlorophaeite on the presence of material resembling phase III only. The justification for basing an identification of chlorophaeite solely on material resembling associated material (A) is equally questionable, as there is the probability that this may be a decomposition product of phase III or of other material present, e.g. ferromagnesian minerals. Thus, phases I, II, and III can be shown to be genetically related, but the origin of the associated material (A) is uncertain and cannot be included within a scheme of nomenclature that comprises interrelated phases of chlorophaeite.

Similarly for palagonite in thin section, material resembling the glassy phase and phases X and Y must be present. The presence of the glassy phase is not critical for identification, as quite frequently all the glass present has been hydrated. Another theory (Bonatti, 1965) is that the magma on extrusion into the sea or under an ice

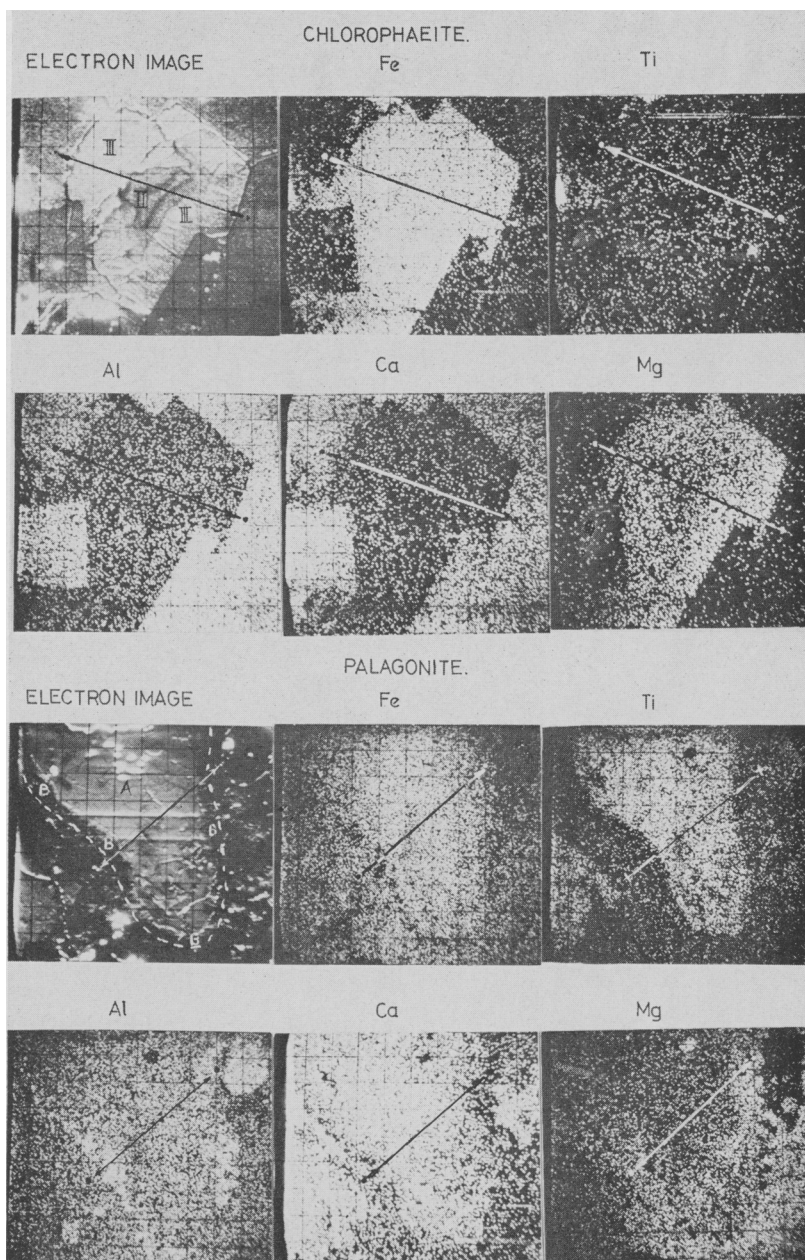


FIG. 8. Electron probe micrographs of neotype chlorophaeite and palagonite. The electron image of chlorophaeite shows phases II and III. The electron image of palagonite shows parent glass (marked A) and phase X (marked B).

sheet may pass straight to palagonite without the formation of basaltic glass as an intermediate. In both cases the effect is the same, no basaltic glass is present, only palagonite. The presence of material resembling either the phase Y or the associated material (M) in isolation also raises a problem in identification. Phase X is a hydrated form of the parent glass. Phase Y is a crystalline form of phase X. Associated material (M) is most probably a decomposition product of phase Y; the final decomposition products are thought to be zeolites and chlorite. The associated material needs characterizing. The main difficulty in such a task is that it must be done *in situ* in the specimen or thin section, as the risk of contamination by another phase of adjacent material, if separation of the phases is attempted, is extremely great. The electron probe at this stage seems to be the most satisfactory instrument for this purpose.

Following the use of the above optical criteria the identity of the material may still be in doubt, in which case further criteria should be applied. Of those remaining, electron probe microanalysis is suggested next; it is appreciated, however, that access to such a machine may not be easy and so X-ray diffraction is also suggested. The X-ray pattern should be compared to those of chlorophaeite and palagonite and it should be immediately obvious which of the two materials the pattern most resembles. Having decided which, the next step would be to compare the pattern of the specimen and standard looking in particular for those lines common to several specimens. Regarding an analysis obtained on the electron probe, it is known that such an analysis is not as accurate as a normal chemical analysis, but the difference between the materials is sufficient to allow them to be distinguished. It is also desirable that more probe analyses of chlorophaeite be obtained.

Further examination of the material under the electron microscope may be necessary after all the above tests have been performed. It is not suggested that any one of these tests is in itself conclusive, but together the author believes that they constitute the most conclusive method at this stage in assessing the character of these materials. It is stressed that more work needs to be done on these materials and it is suggested that the most successful techniques to date are optical microscopy, electron probe microanalysis, X-ray diffraction, and electron microscopy.

Finally three general criteria are included, based upon observations of the specimens obtained by the author: Palagonite is restricted to basic igneous material extruded into water, under ice, or intruded into unconsolidated sediments; chlorophaeite is restricted to basic igneous rocks, which cooled more slowly and which appear to have suffered a period of hydrothermal activity either during late-stage consolidation of the magma or some time after the consolidation of the magma. Green palagonite has never been seen by the author; this suggests that an unstable phase containing ferrous iron does not exist, and lists of previous chemical analyses (Stokes, 1967) show extremely low FeO values for palagonite. Chlorophaeite and palagonite have never been seen together in the same specimen.

Conclusions. Indications that the two materials chlorophaeite and palagonite are different, first suggested by evidence from optical microscopy, are reinforced by further results obtained from the use of other techniques. Chlorophaeite and palagonite

cannot be regarded as simple substances, they are multiphase composites. The presence of certain combinations of these phases or material resembling certain combinations of those phases is suggested as being essential for a positive identification. Some of the techniques employed in the investigations were found to have little value and it is suggested that optical microscopy, X-ray diffraction, and electron probe micro-analysis be considered as the most satisfactory techniques for continued investigations of these materials.

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