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1973/48

THE TRANSFORMATION OF NESQUEHONITE INTO HYDROMAGNESITE

by

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ABSTRACT

Nesquehonite, synthesized in the laboratory, can be readily altered to hydromagnesite via an intermediate phase which is morphologically similar to hydromagnesite. This intermediate phase exhibits an X-ray pattern similar to that of the newly discovered mineral dypingite. The transformation is accompanied by a large loss of water, with resulting increase in magnesium. Chemical analysis indicates that dypingite occurs in a range of phases from slightly altered nesquehonite to hydromagnesite. The alteration of nesquehonite at 52°C is exceedingly rapid, explaining why hydromagnesite is the more common hydrate in nature. This formation of a new mineral via the aqueous phase also occurs in the solid state at temperatures in excess of 100°C, as indicated by Differential Thermal Analysis and Thermal Gravimetric Analysis.

INTRODUCTION

Nesquehonite precipitates from solutions of magnesium bicarbonate below 52°C and hydromagnesite is the stable hydrate above this temperature (Leitmeier, 1915; Dell and Weller, 1959; Kazakov et al., 1959; Langmuir, 1965). However, it has been shown that nesquehonite is an unstable phase (D'Ans et al., 1938; Latimer, 1952; Garrells et al., 1960; Langmuir, 1965). Our interest in this field has stemmed from the following factors.

Hydromagnesite is more common in nature than nesquehonite, even though natural conditions of temperature favour the precipitation of nesquehonite. It is possible therefore that nesquehonite acts as a precursor of some natural hydromagnesites. Disagreement exists over the exact chemical composition of the two minerals (Kazakov et al., 1959; Morandi, 1969), suggesting that workers are discussing different compounds, or that the minerals vary in composition. As nesquehonite precipitates under different conditions from hydromagnesite (Kasakov et al., 1959), a knowledge of the requisite conditions for the transformation and for any intermediate phases is important to the understanding of diagenesis of carbonates.

Some of the above factors are being investigated as part of our program encompassing the biological and abiological precipitation, decomposition, and diagenesis of carbonates. The object of the present work has been to prepare nesquehonite under well defined conditions, to document its decomposition, and to investigate the mineral phases produced.

PREPARATION OF NESQUEHONITE

Nesquehonite (Fig. 1A) was prepared both biologically and abiologically (Davies and Bubela, in prep.) from saturated Mg $(HCO_3)_2$ solutions. The resultant precipitate was harvested, analysed, and identified.

DISSOCIATION OF NESQUEHONITE AT 52°C

Nesquehonite crystals were placed in a vessel containing distilled water, sealed, and placed into a water bath kept at a constant temperature of 52°C. After 72 hours the crystals were examined by X-ray diffraction and scanning electron microscope. The nesquehonite had partly dissolved (Fig. 2A) and pods of plate-like crystals had formed (Figs. 1B and 2B).

This new mineral phase was characterized by X-ray diffraction (XRD) patterns (Fig. 3) which in some respects resembled both nesquehonite and hydromagnesite, but which included diffraction peaks absent from the XRD patterns of these minerals. The new mineral was provisionally named protohydromagnesite. After a period of a week at 52°C the proportion of protohydromagnesite to nesquehonite had considerably increased.

ANALYSIS OF NESQUEHONITE, PROTOHYDROMAGNESITE, AND HYDROMAGNESITE

The chemical analysis of the synthesized nesquehonite (Table 1) shows that the mole proportions are very close to

1.0 MgO : 1.0 CO_2 : $3H_2O$, the same as the normally quoted formula for nesquehonite. The closeness of the approximation is illustrated in Fig. 4, in which the compositions of common magnesium carbonates and of those synthesized during the present work are plotted. From the analysis of the protohydromagnesite (Table 1) the exact mole proportions are 0.80 MgO : 0.75 CO_2 : 1.89 H_2O. Therefore the formation of protohydromagnesite from nesquehonite represents a loss of H_2O and a slight gain of CO_2 relative to MgO.

The Differential Thermal Analysis (DTA) graph (Fig. 5A) for nesquehonite shows major endothermic reactions occurring at 116°, 150°, 480°, and 520°C. A small shoulder occurs at 180° while broader shoulders occur at 400°-436° and 470°C. A major exothermic reaction is seen at 484°C. The end product X-rayed as periclase. The DTA graph for protohydromagnesite (Fig. 5B) shows endothermic reactions occurring at 56°, 84°, 130°, 260°-286°, 348°-384°, 480°, and 516°C. Hydromagnesite exhibits endothermic reactions (Fig. 5C) at 270°, 378°, 476°, and at approximately 500°C. An exothermic reaction is seen at 484°C. Shoulders can be observed on the graph at 320° and 410°-450°C.

The Thermal Gravimetric Analysis (TGA) of nesquehonite (Fig. 5A) shows the following features: a 29% loss of weight occurs by 200°; further losses take place in the temperature ranges 200°-480° (from 29% to 51%), and 480°-530° (20%); the total loss equals 71.3%.

The results of TGA of protohydromagnesite (Fig. 5B) indicate that the loss of weight begins at 32° and reaches a total weight loss of 60.8% at 525°C. Shoulders can be seen on the TGA graph at 130° and 286°C by which temperatures the losses amounted to 4.5% and 15.4% respectively. The TGA for synthetic hydromagnesite (Fig. 5C) shows a loss of 9% at 270° and 13% at 320°C. A total weight loss of 72.6% is apparent, after which the residue X-rayed as periclase.

DISCUSSION

The mineral provisionally named by us as protohydromagnesite was found to have a diffraction pattern very similar to the mineral dypingite (Fig. 3) recently discovered in nature by Raade (1970). In terms of physical properties, however, they are very different. Raade (op. cit., p.1458) says: "Dypingite forms white globular aggregates ...... radiating aggregates consisting of fibres"; this accurately describes the precipitated nesquehonite (Fig. 1A) but does not fit the resultant protohydromagnesite (Fig. 2B). Dell and Weller (1959) note that the dry transformation of nesquehonite into hydromagnesite occurred experimentally without any change in morphology. This process may operate during the formation of the mineral described by Raade, who states that dypingite is a mineral closely related to hydromagnesite, which is monoclinic and normally forms curved plates rather than radiating needles. Both the hydromagnesite and protohydromagnesite produced in our laboratory formed as curved plates. This further suggests that the mineral described by Raade may have formed by the alteration of nesquehonite, which itself is a transitory mineral.

The chemical analysis of the synthetic nesquehonite confirms that the mineral contains only one molecule of MgO, not two as suggested by Morandi (1969). Comparing its chemical analysis with nesquehonite, protohydromagnesite represents a loss of H_2O and slight gain of CO_2 relative to MgO. If the loss of water is expressed as a loss from nesquehonite, then it represents 0.4 moles, or 5.5 mole %. As the formula percent calculated from simple mole proportions is very close to the analytical results, it indicates that the chemical formula for protohydromagnesite is a simple multiple of the mole proportions shown in Table 1. This is 1 MgO : 1 CO_2 : $2H_2O$. This is different from the formula published by Raade for natural dypingite which was given as 4.6 MgO : 4 CO_2 : 6.12 H_2O. The triangular plots of Raade's dypingite and our protohydromagnesite are shown in Fig. 4. As the two show very similar XRD patterns, it is apparent that mineral phases similar to dypingite occur over a wide compositional range, largely as a result of differences in the percentage H_2O content. It is doubtful, therefore, whether dypingite can be characterized by an exact chemical formula. The new mineral described by Raade is probably only one stage in the decomposition course of nesquehonite.

Published formulae for hydromagnesite resolve into two groups:

a. 5 MgO : $4CO_2$: $5H_2O$ (Morandi, 1969; Raade, 1970)

b. 4 MgO : 3 CO_2 : $4H_2O$ (Leitmeier, 1915; Palache et al., 1951; Langmuier, 1965)

The formula percentages for these three oxides obtained from the above are shown in the lower part of Table 1. The analysis of synthetic hydromagnesite shows a deficiency in MgO, and a little excess CO_2 and H_2O. It is therefore difficult to compute an exact formula. The best approximation, however, would be 3 MgO : $3CO_2$: $4H_2O$. This formula plots reasonably close (Fig. 4) to formula (b) shown above. The chemical analysis of synthetic hydromagnesite (upper part of Table 1) indicates a progression from nesquehonite to protohydromagnesite and finally to hydromagnesite, with a relative increase of MgO and decrease of H_2O content.

The loss of water molecules from nesquehonite at raised temperatures can be followed by comparing the DTA and TGA curves. The endotherm at 116°C corresponds with a 10% total weight loss. Since 1 molecule of H_2O represents 13%, it is presumed that almost one molecule of H_2O is lost during this endothermic reaction. Similarly by 150°, a 20% weight loss and by 200°C a 29% loss occurred. As the total loss represents approximately 2.5 molecules of water, some water therefore must be lost in the temperature range 200°-500°C.

Published DTA curves are shown in Fig. 6. All curves show major endothermic reactions occurring below 250°C. Dell and Weller (1959), Beck (1950), and Kozakov et al., (1959) report that two molecules of water are lost below this temperature. Dell and Weller (op. cit.) and Kazakov et al., (op. cit.) suggest the possibility of the formation of a new hydrate after the loss of the first water molecule. Morandi (1969) considers that four H_2O molecules are lost below 200°C. Morandi's DTA curve approximates closest to our work. In the range 250°-450°C the curves published by these workers show similar decomposition characteristics, the major feature being the endothermic reaction at around 400-450°C. All authors except Kazakov et al., agree that CO_2 is liberated at this temperature; Kazakov et al., consider that (OH) groups are liberated. DTA curves published by Brousse and Guerin (1966) (Fig. 6C) differ from the previously mentioned results mainly by the presence of an endothermic reaction at 310°C. It is noted below that an endotherm at about that temperature occurs in protohydromagnesite.

The reactions detected by the DTA on protohydromagnesite are seen in the curve published by Raade (1970) for dypingite. The major difference is the position of the exotherm. Our DTA and TGA curves for protohydromagnesite (Fig. 5B) show an excellent correlation; the shoulder at 130°C corresponding with the end of an endothermic reaction. By this time a 4.5% weight loss has occurred. The top of the 286° shoulder correlates with the 286° endothermic reaction, by which time 15.4% by weight has been lost. If this loss represents loss of H_2O, then 1.5 moles have been lost at this stage. The top of a shoulder at 400°C corresponds again with the end of an endothermic reaction. The weight loss is 29%. All water therefore has been removed. The final weight loss is approximately 30% at 400°-425°C. This loss is probably due to a release of CO_2.

It should be noted in the data published by Raade (1970) that the positions of major weight losses (TGA) do not correspond with major reactions as shown on the DTA.

When comparing DTA curves for natural nesquehonite (Brousse and Guerin, 1966) with our curves for protohydromagnesite and synthetic nesquehonite the following features are apparent. The curves for natural and synthetic nesquehonite are similar except for the endotherm at 310°C. This endotherm is not far removed from a similar reaction occurring at 290° in protohydromagnesite. When the results of chemical analysis of the natural nesquehonite (Brousse and Guerin, 1966) are recalculated and plotted as shown in Table 1 and Fig. 4, the natural nesquehonite is placed in an intermediate position between protohydromagnesite and synthetic nesquehonite. This further evidence for a gradual change of nesquehonite is supported by the extra endothermic peak on the DTA curve. We suggest that natural nesquehonite is changing into protohydromagnesite, an intermediate phase similar to dypingite.

The DTA and TGA curves for hydromagnesite indicate a loss of approximately 3 molecules of water during an endothermic reaction at 270°C. As hydromagnesite is a hydroxycarbonate, the endothermic reaction at 378°C is almost certainly due to release of (OH). The endothermic peak at 270°C coincides approximately with the peak for dypingite described by Raade (1970). If this reaction is the final release of water, then the progression to lower temperature indicates that structural water is progressively more easily released in the series nesquehonite to hydromagnesite.

CONCLUSION

It is our contention that nesquehonite alters to hydromagnesite via a number of intermediate phases. An early phase is the nesquehonite reported by Brousse and Guerin. A more advanced stage is the protohydromagnesite synthesized by the authors. The X-ray analysis shows that this is crystallographically very similar to dypingite reported by Raade (1970). The latter mineral is therefore a further stage in the nesquehonite → hydromagnesite transformation. A whole series of dypingite-like phases occur as intermediates between the two end members.

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TABLE 1. Chemical compositions of common magnesium carbonates hydrates, and those synthesized during present work.

*) Chemical formulae were obtained from Kazakov et al., (1959), Langmuir (1965), Morandi (1969), and Raade (1970).

ANALYSIS %		RECALC. TO 100%	MOLE PROPORTIONS		MOLE %	FORMULA %
NESQUEHONITE: (DAVIES and BUBELA)						
MgO	27.59	28.154	0.698	1	19.23	28.2
CO_2	31.61	32.254	0.733	1.05	20.20	33.6
H_2O	38.80	39.592	2.198	3.15	60.56	38.1
NESQUEHONITE: (BROUSSE and GUERIN, 1966)						
MgO	27.66	28.645	0.710	1	20.02	28.2
CO_2	33.08	34.258	0.778	1.10	21.94	33.6
H_2O	35.82	37.096	2.059	2.90	58.03	38.1
PROTOHYDROMAGNESITE:						
MgO	29.97	32.197	0.799	1.0	23.03	32.4
CO_2	30.80	33.200	0.754	0.94	21.76	38.6
H_2O	32.00	34.494	1.915	2.40	55.22	28.9
HYDROMAGNESITE:						
MgO	37.48	38.576	0.957	1.0	31.22	38.0
CO_2	38.58	39.708	0.902	0.94	29.44	45.3
H_2O	21.10	21.717	1.205	1.26	39.34	17.0

COMMON HYDRATES *)

NAME	FORMULA	MOLE %	FORMULA %
MAGNESITE	$MgO : CO_2$	50 : 50	47.7 : 52.3
BARRINGTONITE	$MgO : CO_2 : 2H_2O$	25 : 25 : 50	33.3 : 36.7 : 30
NESQUEHONITE	$MgO : CO_2 : 3H_2O$	20 : 20 : 60	29.0 : 31.9 : 39.1
LANSFORDITE	$MgO : CO_2 : 5H_2O$	14.3 : 14.3 : 71.4	23 : 25.3 : 51.7
ARTINITE	$2MgO : CO_2 : 4H_2O$	28.6 : 14.3 : 57.2	40.8 : 22.4 : 36.8
HYDROMAGNESITE (a)	$5MgO : 4CO_2 : 4H_2O$	35.7 : 28.6 : 35.7	44.3 : 39.3 : 16.2
HYDROMAGNESITE (b)	$4MgO : 3CO_2 : 4H_2O$	36.2 : 27.3 : 36.2	44.0 : 36.2 : 19.8
DYPINGITE	$5MgO : 4CO_2 : 6H_2O$	33.4 : 26.6 : 40	41.4 : 36.4 : 22.2

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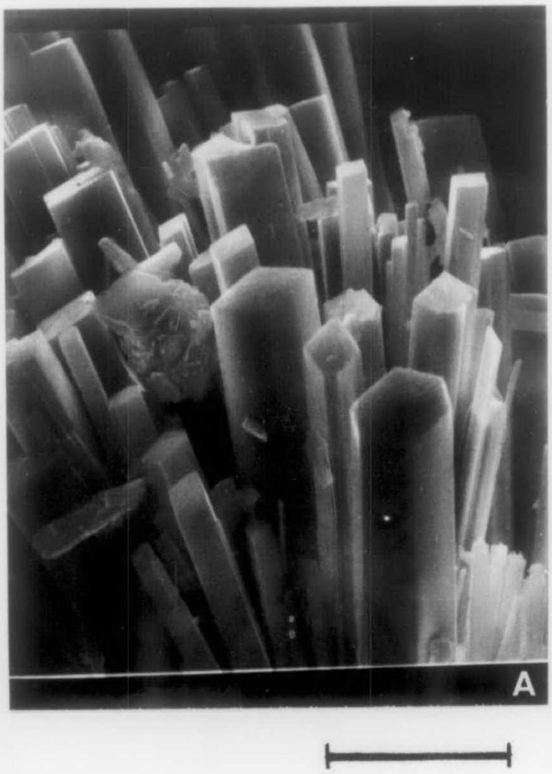
Fig. 1. A. Nesquehonite crystals.

B. Protohydromagnesite bundles growing amidst nesquehonite crystals.

Scale Bar = 30 μ.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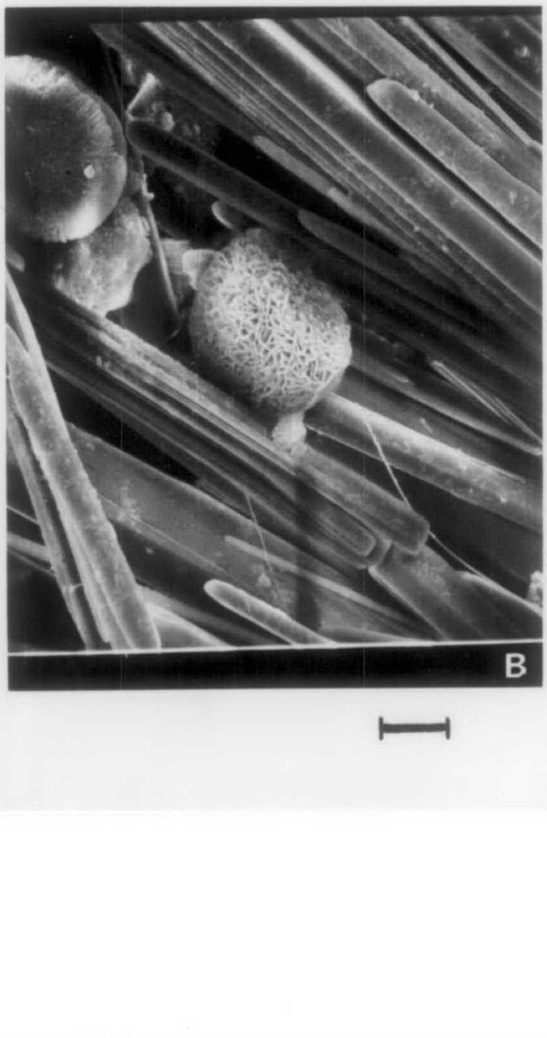
B

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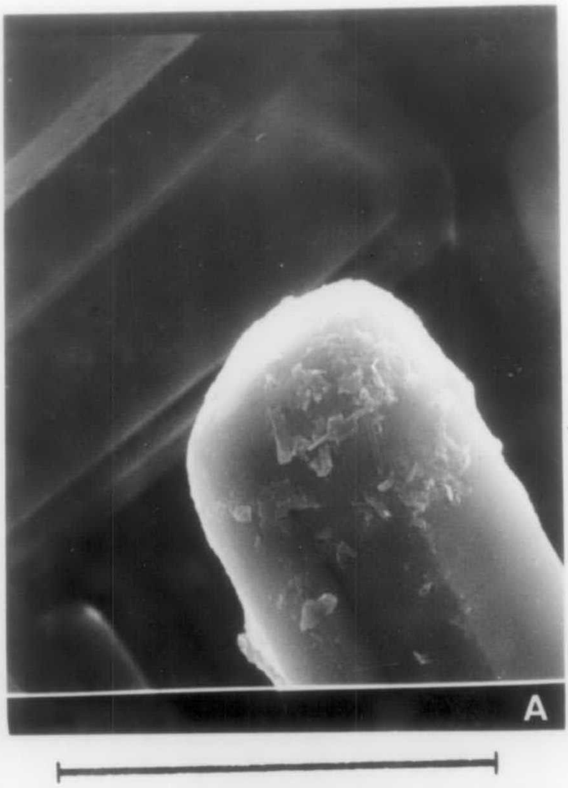
Negative No. GA/7750

Fig. 2. A. Nesquehonite crystal undergoing solution prior to reprecipitation as protohydromagnesite.

B. Protohydromagnesite

Scale Bar = 30 μ.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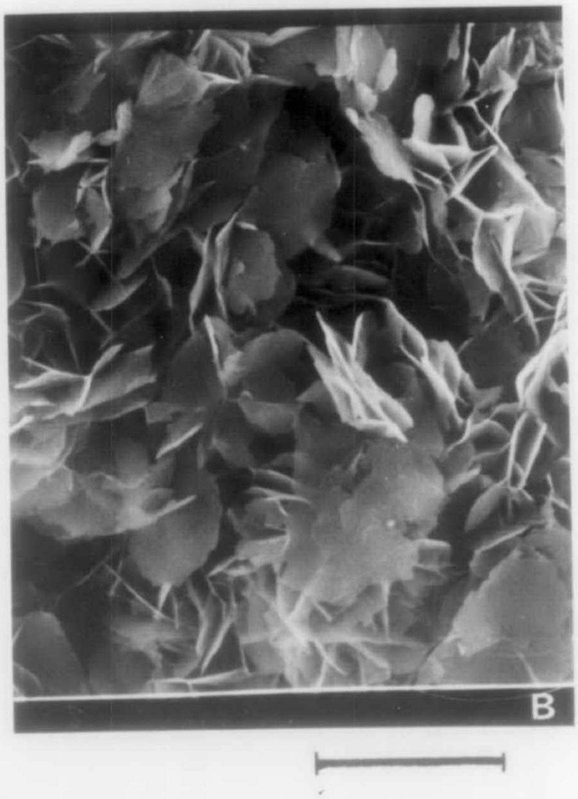
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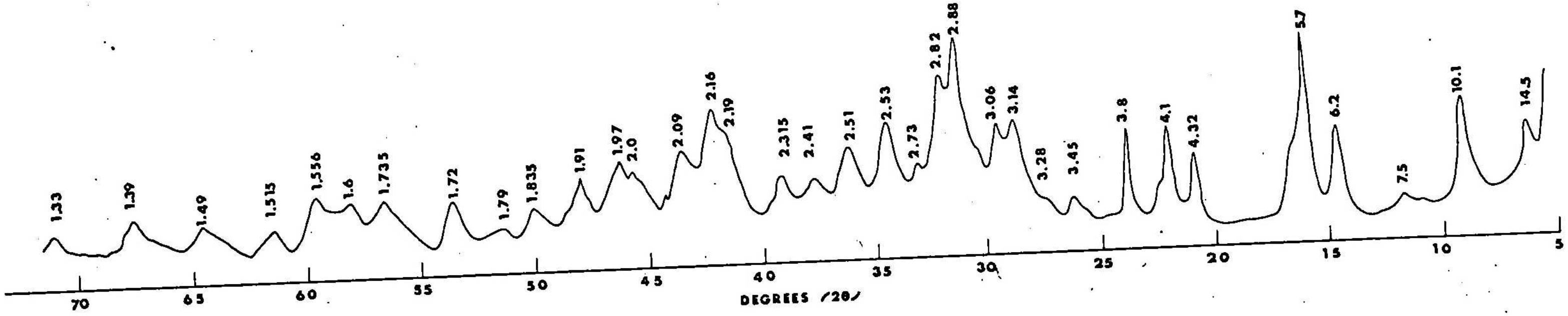
Fig. 3. X-ray diffraction pattern of protohydromagnesite.

Fig 3.


1.33
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1.49
1.515
1.556
1.6
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1.72
1.79
1.835
1.91
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2.0
2.09
2.16
2.19
2.315
2.41
2.51
2.53
2.73
2.82
2.88
3.06
3.14
3.28
3.45
3.8
4.1
4.32
5.7
6.2
7.5
10.1
14.5
70
65
60
55
50
45
40
35
30
25
20
15
10
5
DEGREES (2θ)

Fig. 4. Triangular plot of compositional characters of common magnesium carbonates hydrates, and those synthesized during the present work.

FIG 4

Fig 4

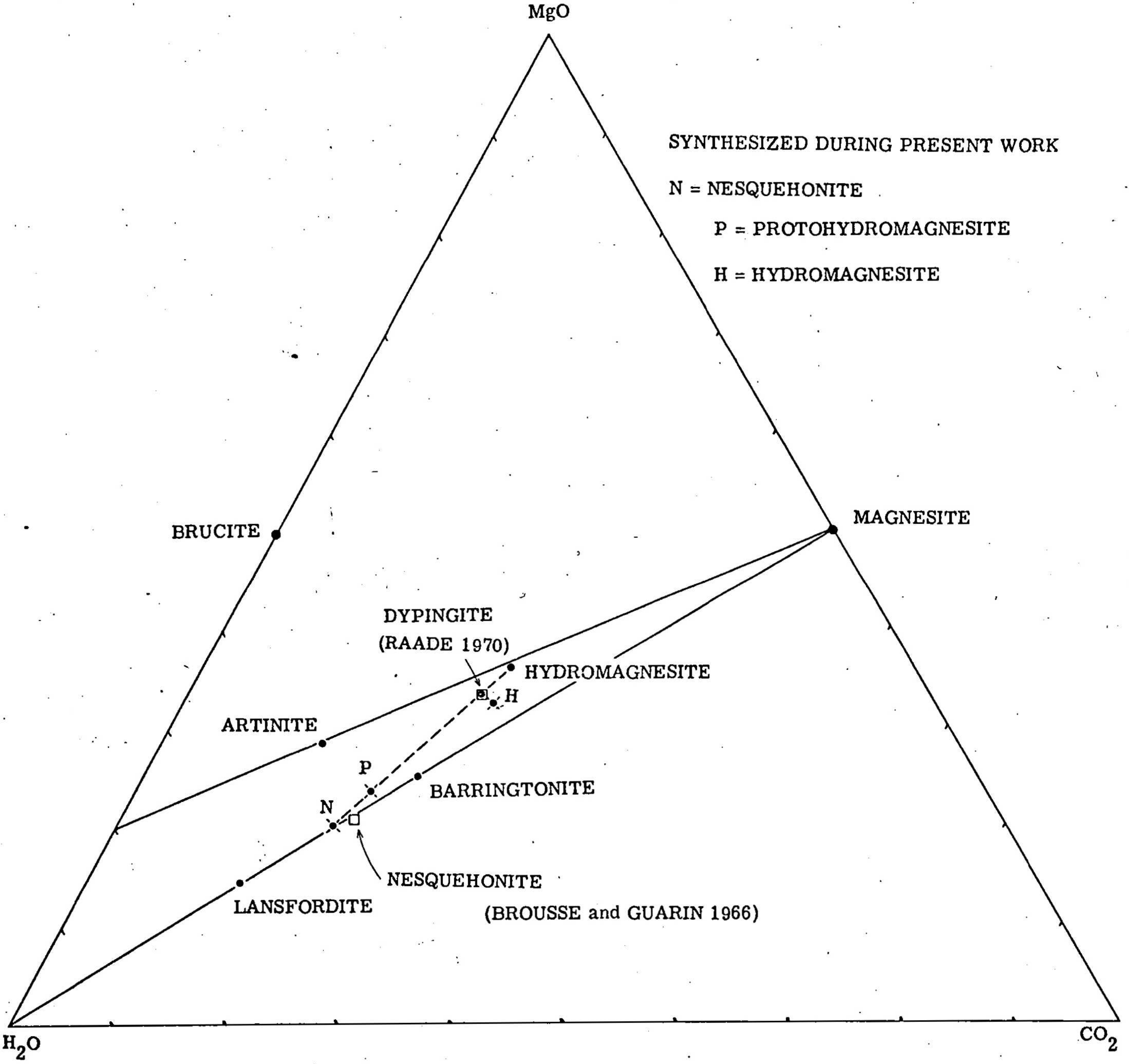

MgO
SYNTHESIZED DURING PRESENT WORK
N = NESQUEHONITE
P = PROTOHYDROMAGNESITE
H = HYDROMAGNESITE
BRUCITE
MAGNESITE
DYPINGITE
(RAADE 1970)
HYDROMAGNESITE
H
ARTINITE
P
BARRINGTONITE
N
NESQUEHONITE
(BROUSSE and GUARIN 1966)
LANSFORDITE
H_2O
CO_2

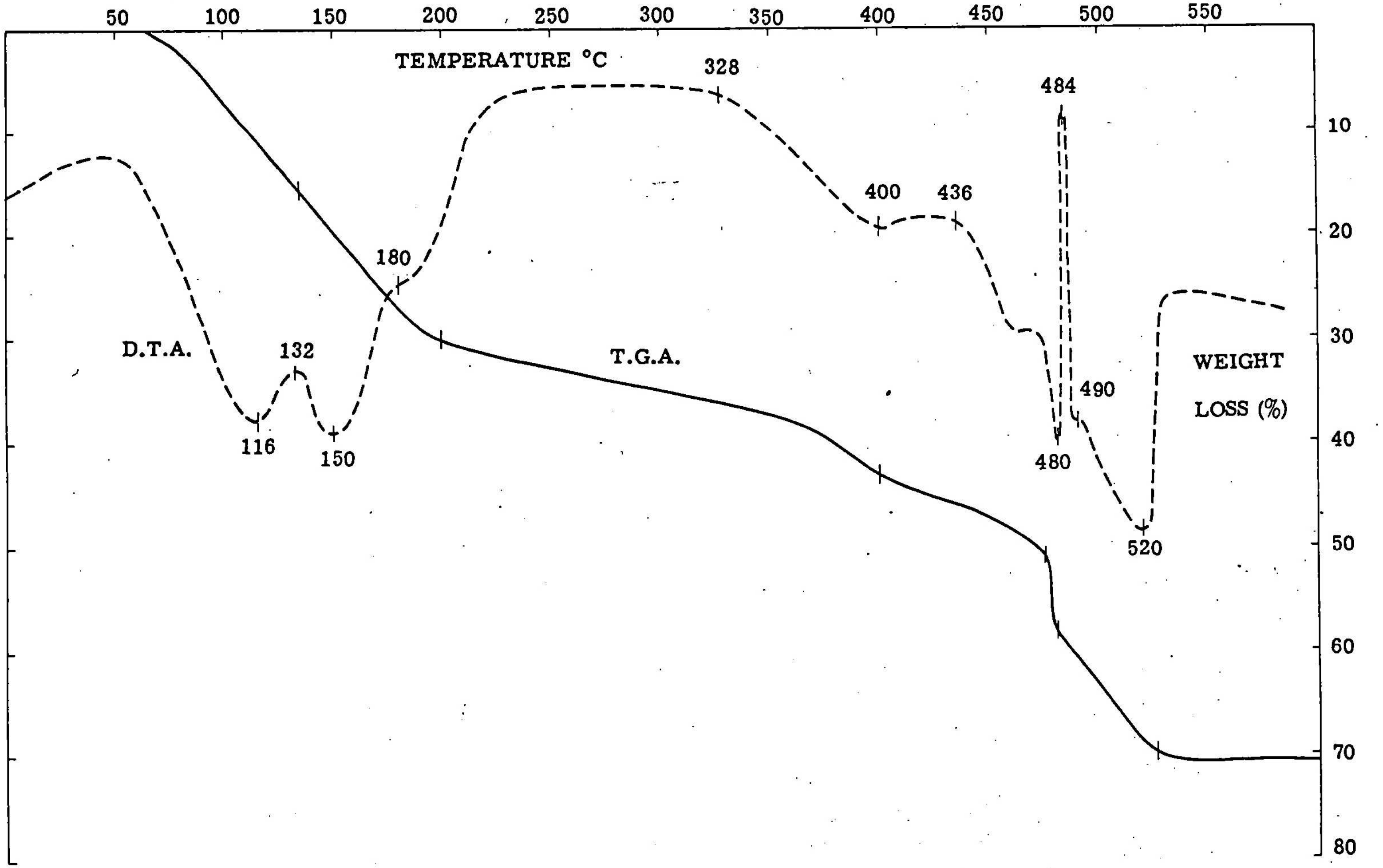
Fig. 5. Differential thermal analysis and thermogravimetric analysis curves.

A. Nesquehonite.

B. Protohydromagnesite.

C. Hydromagnesite.

Fig 5a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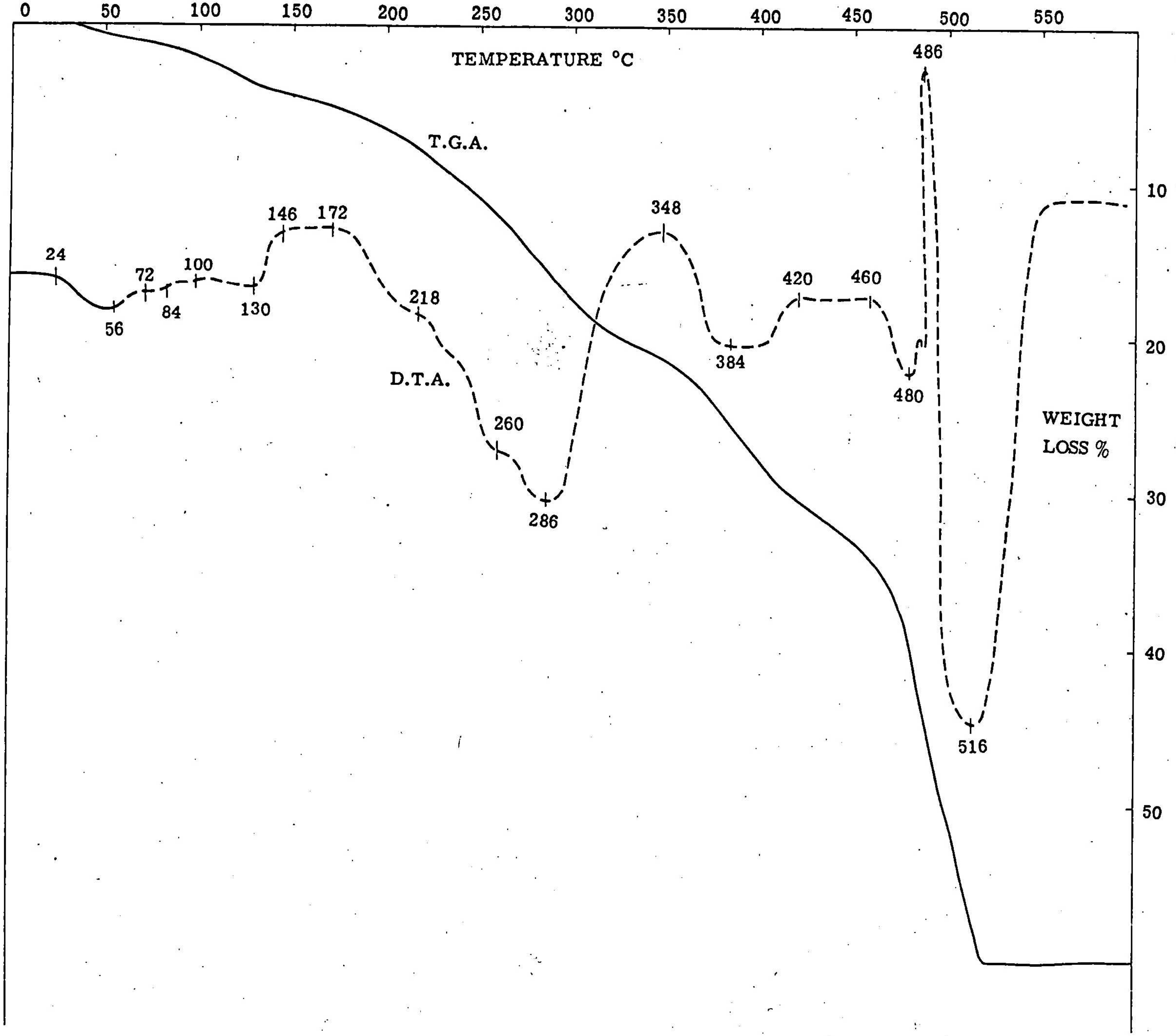
100
150
200
250
300
350
400
450
500
550
TEMPERATURE °C
328
484
400
436
180
D.T.A.
132
T.G.A.
116
150
490
480
520
WEIGHT
LOSS (%)
10
20
30
40
50
60
70
80

Fig 5B

Fig 5b


0
50
100
150
200
250
300
350
400
450
500
550
TEMPERATURE °C
T.G.A.
D.T.A.
24
56
72
84
100
130
146
172
218
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286
348
384
420
460
480
486
516
10
20
30
40
50
WEIGHT
LOSS %

Fig 5c

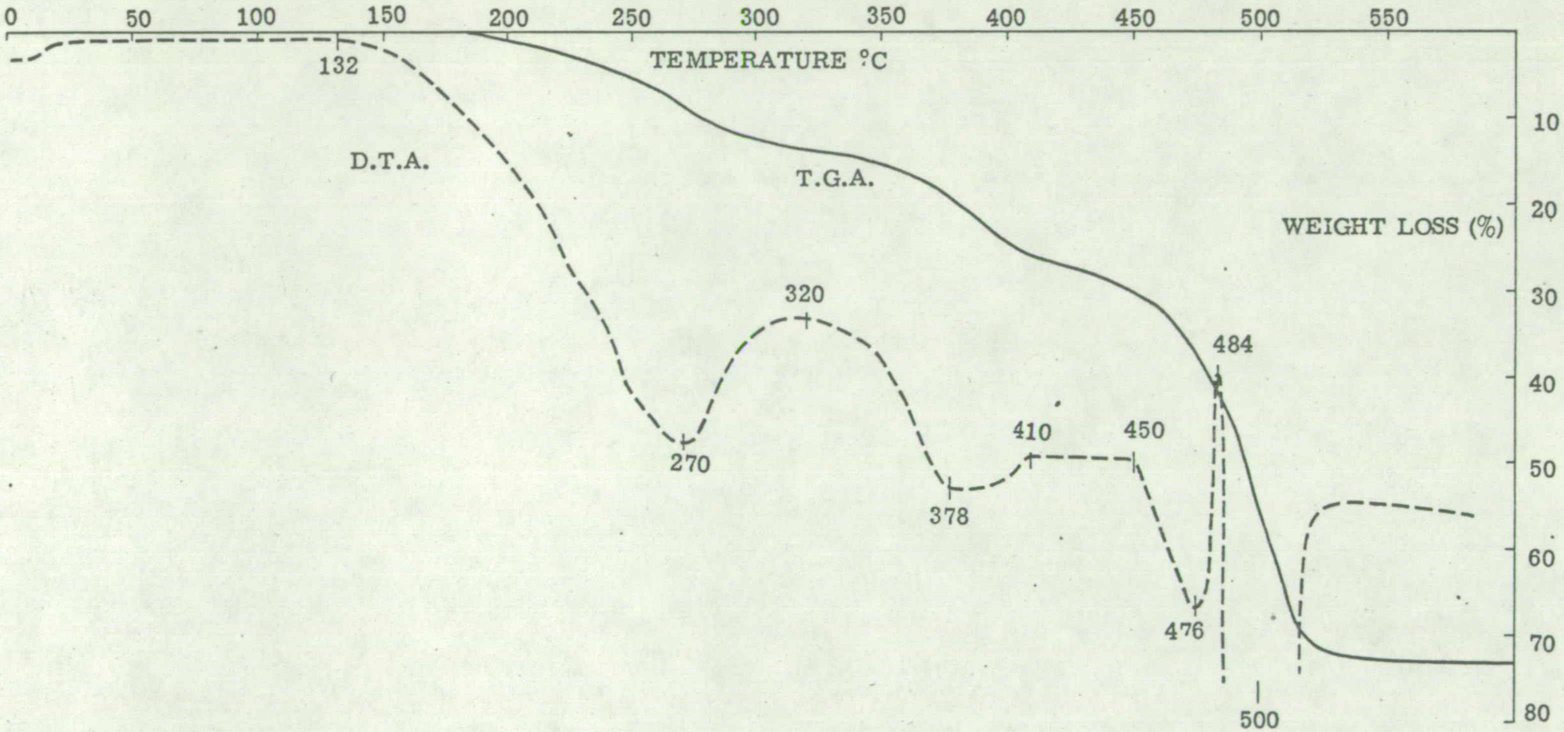
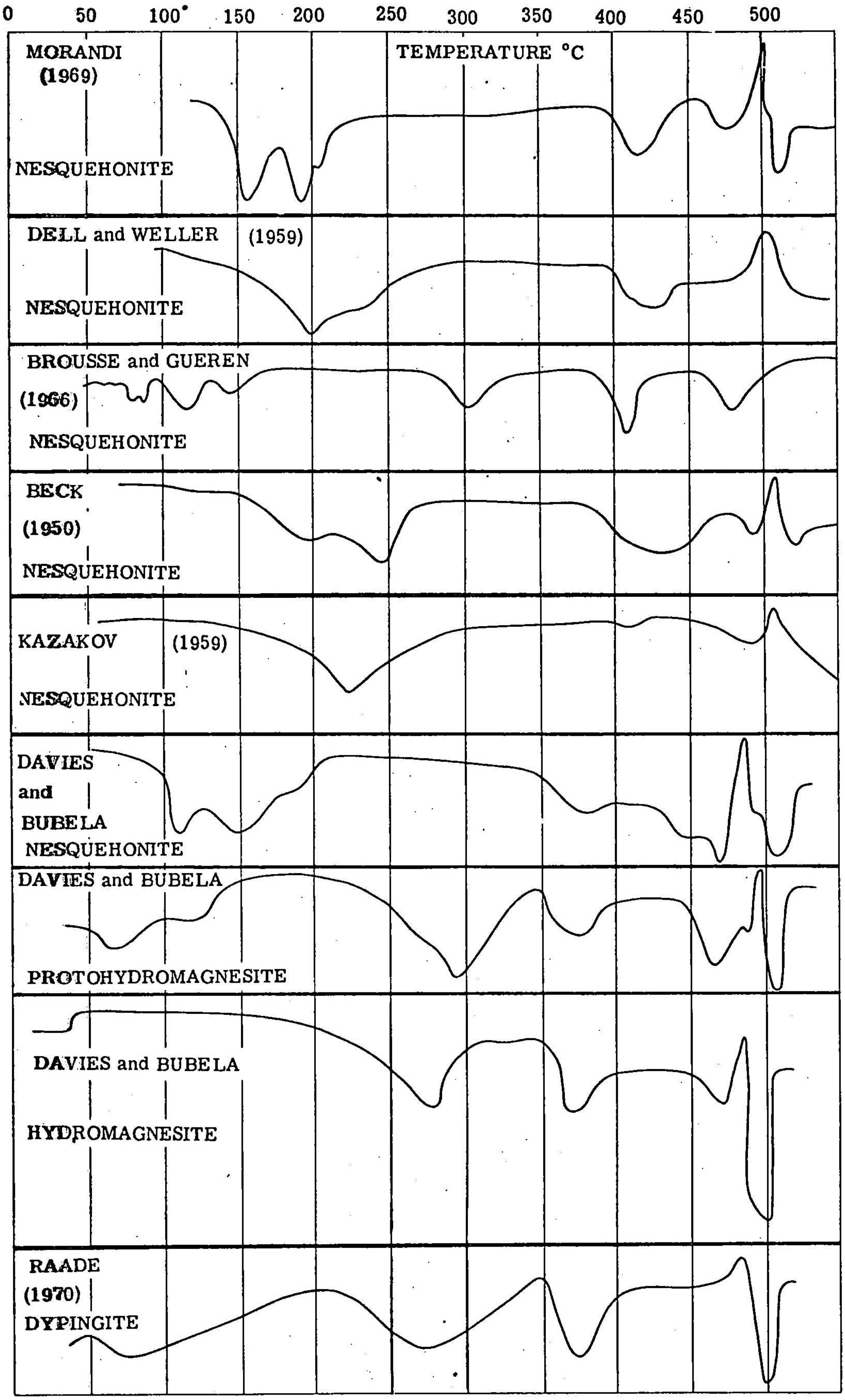

0
50
100
150
200
250
300
350
400
450
500
550
TEMPERATURE °C
132
D.T.A.
T.G.A.
WEIGHT LOSS (%)
10
20
30
40
50
60
70
80
320
270
410
450
378
484
476
500

Fig. 6. Differential thermal analysis curves.

Fig 6


0
50
100
150
200
250
300
350
400
450
500
TEMPERATURE °C
MORANDI
(1969)
NESQUEHONITE
DELL and WELLER
(1959)
NESQUEHONITE
BROUSSE and GUEREN
(1966)
NESQUEHONITE
BECK
(1950)
NESQUEHONITE
KAZAKOV
(1959)
NESQUEHONITE
DAVIES
and
BUBELA
NESQUEHONITE
DAVIES and BUBELA
PROTOHYDROMAGNESITE
DAVIES and BUBELA
HYDROMAGNESITE
RAADE
(1970)
DYPINGITE