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THE THERMOCHEMISTRY OF SOME IRON PHOSPHATE MINERALS: VIVIANITE, METAVIVIANITE, BARAĆITE, LUDLAMITE AND VIVIANITE/METAVIVIANITE ADMIXTURES

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ABSTRACT

Vivianite shows a major differential thermal response spanning 65 to 315°C attributable to an endothermal loss of structural water combined with the oxidation of Fe^{2+} (which results in exothermic peak(s) being described within the endothermal record) and consequential breakdown of the original structure. Subsequently, a gradual sintering of the amorphous product culminates in an exothermic structural ordering at 660°C resulting in the formation of α-$FePO_4$, $Fe(PO_3)_3$ and, occasionally, Fe_2O_3. The cause of a small exotherm near 780°C is possibly similar; decomposition/melting occurring between 1000 and 1200°C. Metavivianite behaves similarly but with the initial dehydration record being less complicated by oxidation of iron and with small endotherms forming just above 320°C from dehydroxylation of the structure. Baraćite also has the same basic pattern but an additional exotherm near 700°C, possibly due to formation of high magnesium phosphate. Ludlamite shows a narrower dehydration endotherm at a higher temperature reflecting the difference in bond type between the parallel bands of octahedra in the two structures. The differences in thermal behaviour between vivianite and metavivianite are too slight to allow them to be used to detect the presence of one mineral in the other with any reliability. While oxidation of vivianite might exert some influence on the response of the mineral to heat, other factors such as grain size and instrumentation differences are believed to have a greater influence on dissimilarities between published results.

INTRODUCTION

Several thermal analytical studies of vivianite have been published which provide apparently inconsistent results [1–8]. Data reported on Scifax thermal data cards [9] for both natural and synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$ could well have come from two quite unrelated substances. Henderson et al. [8] have suggested that a major factor contributing towards such imprecise results has been a failure to standardise experimental conditions. However, many so-called "vivianite" samples are proving to be vivianite/metavivianite admixtures [7,8,10]. The varying degrees of oxidation, hydration and hydroxylation is reflected in the varying thermal response of differing samples. Dormann et al. [7] have explored this variation with a limited range

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of samples. The present study presents additional data obtained under standard conditions for vivianites (sensu stricto) and for vivianite/metavivianite admixtures from a number of world localities and makes some comparisons with similarly derived thermal responses for metavivianite, baraćite and ludlamite.

INSTRUMENTATION AND CONDITIONS

All determinations were made using either a Shimadzu DT-2B thermal analyser incorporating 4 $Pt-Pt_{90}Rh_{10}$ thermocouples (0.5mm o.d.) arranged at 90°, or a Shimadzu DGT-2B thermobalance with differential recording facility and incorporating 3 $Pt-Pt_{90}Rh_{10}$ thermocouples (0.5mm o.d. at 120°). Sample crucibles were 6 mm o.d. × 17 mm held in a beryllia holder.

Several previous studies of vivianite have employed inert gases or vacuum systems [3,7]. Conditions for the present analyses were deliberately chosen as being able to be easily duplicated in a conventional thermal analytical laboratory without recourse to specialised equipment [11]. These were: amount of sample—100 to 150 mg mixed with 20 mg Al_2O_3; reference material—100mg ignited and annealed Al_2O_3; treatment of sample—fine ground (100–200 μm) in agate mortar, loose packed, no tamping; heating rate—10° min^{-1} after 80°C; furnace atmosphere—air, no turbulence.

TERMINOLOGY AND SAMPLES

Vivianite (sensu stricto) is the mineral $Fe_3(PO_4)_2 \cdot 8H_2O$ [12]. In most museum and laboratory specimens some oxidation of iron has occurred and the formula approximates closely to $Fe^{2+}_{3-x}Fe^{3+}_x(PO_4)_2(OH)_x(8-x)H_2O$ where $x < 1.2$ [13–15]. Usually, when more than 40% of the iron has been oxidised the monoclinic vivianite lattice collapses to the triclinic symmetry of metavivianite [7,15]; the formula remaining as $Fe^{2+}_{3-x}Fe^{3+}_x(PO_4)_2(OH)_x$ $(8-x)H_2O$ with $x > 1.2$.

Baraćite is $(Mg,Fe)_3(PO_4)_2 \cdot 8H_2O$ with Mg > Fe and of the same space group as vivianite, unlike bobierrite [16]. Ludlamite is $Fe_3(PO_4)_2 \cdot 4H_2O$ [12].

It has become increasingly apparent that numerous samples examined and reported in many of the previous studies of "vivianite" are in fact mixtures of vivianite and metavivianite [7,8,11,15]. Further, it would also appear that the boundary between monoclinic vivianite and triclinic metavivianite cannot be defined simply by chemical considerations, as the extent of oxidation of iron [7,10,15]. The figure of 1.2 atoms Fe^{3+} given above does not always apply and factors such as crystal size and degree of crystallinity appear to play a role in the stability of the monoclinic species

[8,10]. In the present study, all samples referred to as "vivianite" display the X-ray signature of the monoclinic lattice only [10]. Some degree of oxidation is evident in all such samples and their formulae is best given in the ferrous/ferric form shown above. The qualification "oxidised vivianite" will not be used as this merely obfuscates matters.

Where the X-ray pattern of a sample also shows the signature of the triclinic lattice, the specimen is referred to here as a "vivianite/metavivianite admixture", although Sameshima et al. [10] have indicated that a third iron phosphate phase may also be present.

Samples were supplied by the Department of Geology, University of Auckland, the Department of Mineralogy, British Museum (Natural History), and the Smithsonian Institution, U.S. National Museum. Where sample numbers are used in the text and figures they are prefixed by AU, BM, or US to denote their respective origin.

Most of the coarsely crystalline specimens supplied proved to be vivianite/metavivianite admixtures including that from Anloua, Cameroons. Bocchi et al. [5] and Dormann et al. [7] studied specimens from this locality that proved to be monomineralic vivianite. Sameshima et al. [10] reported two specimens from Ashio Mine, Japan, one of which was vivianite alone but the other was the admixture. These facts underline the need for workers to ensure the precise nature of a particular "vivianite" specimen being studied, particularly as present experience is that museum specimens readily undergo alteration of their crystal chemistry with time.

All samples were carefully handpicked and subjected to X-ray analysis to check for possible contaminants such as those reported by Henderson et al. [8] during their trace element studies. However, contamination from siliceous diatoms seems likely in some earthy samples from New Zealand [17], although these do not appear to have affected the thermal results.

Both the ludlamite and baraćite specimens were rather small and were run as received, being given no pre-treatment other than grinding. Both samples showed a moderate broad low temperature endothermic event which is attributed to the expulsion of absorbed moisture. The size of the samples precluded detailed studies being made as to the nature of the decomposition products as was done for vivianite, and the interpretations given here of the thermal responses recorded for these two minerals are quite tentative.

Some fifty mineral samples from various localities were analysed. The results shown here are from the following specimens and are given by way of example: synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$ as discussed by Sameshima et al. ref. 10, Table I, col. 5; earthy vivianite, AU321—Hunua, New Zealand, cf. Henderson et al. [8]; earthy vivianite, AU325—Wairoa Falls, New Zealand, cf. Rodgers [18] and Henderson et al. [8]; nodular, acicular, crystalline vivianite, AU2469, Styak's Swamp 90 ft. below surface, New Zealand, cf. Rodgers [18] and Henderson et al. [8]; coarsely crystalline vivianite/metavivianite admixture AU322, Millerton, New Zealand, cf. Henderson et al. [8]; earthy vivianite/metavivianite admixture AU2796, top of Hope Saddle, South Island, New Zealand, cf. Henderson et al. [8]; crystalline vivianite/metavivianite admixture AU2773, Ashio Mine, Tochigi Prefecture, Japan, cf. Sameshima et al. [10]; crystalline vivianite/metavivianite admixture US96424, AU2778, Monmouth Co., New Jersey, cf. Sameshima et al. [10]; crystalline vivianite/metavivianite admixture BM1962 413, Anloua, Cameroons, cf. Sameshima et al. [10]; metavivianite US127100 (type specimen) Big Chief Quarry, South Dakota, cf. Rodgers and Johnston [19], who give the formula as $Fe^{2+}_{1.14}Fe^{3+}_{1.86}(PO_4)_2(OH)_{1.86}6.1H_2O$; baraćite AU2553, Blow River, Yukon, cf. Sturman and Mandarino [16]; ludlamite, BM1972 462, AU2792, Cobalt, Lembi Co., Idaho.

VIVIANITE

All vivianite samples examined in the present study show a major thermal event involving strong endothermic reactions, with a maximum response in the region of 187 to 260°C (Fig. 1). The thermogram starts to inflect between 67 and 117°C where, presumably, absorbed water is lost; X-ray diffraction patterns taken of samples before and after this initial heating show no appreciable structural change up to 150°C and, in one case, 190°C. The total event is complex and varies between samples, being recorded as a series of subpeaks and shoulders on the sides of a dominant endothermic peak which terminates around 267–317°C. At this stage the product has become X-ray amorphous.

All previous differential thermal studies of "vivianite" have recorded a similar event (Fig. 2) and it has generally been attributed to expulsion of structural water [1–8]. However, of these studies only three [5,7,8] have indisputably studied vivianite (sensu stricto) and, it so happens, that these workers differ from those of previous studies in interpreting the record of the event as a continuous, unstaged, endothermal dehydration overwritten by a concomitant, continuous, unstaged, exothermal oxidation of Fe^{2+}.

The earlier studies tended to be preoccupied with trying to relate the area under the various subpeaks and shoulders to staged losses of differing numbers of water molecules. For example, Manly [1] reported a 5–2–1 pattern of loss of the water molecules with maxima for each stage occurring at 260, 330 and 380°C. Anderson et al. [2] favoured a 3–5 loss and, while Kleber et al. [3] recognised that the total pattern of the event, both in the differential and the thermogravimetric record, was complicated by the oxidation of iron, they believed they could recognise a 5–2–1 loss pattern.

Bocchi et al. [5] were the first to show that the water loss was a continuous process and no stages could be recognised in the overall pattern. Dormann et al. [7] concurred, and these workers regarded the development of endothermal subpeaks "semble lié à l'oxydation du fer associée à la

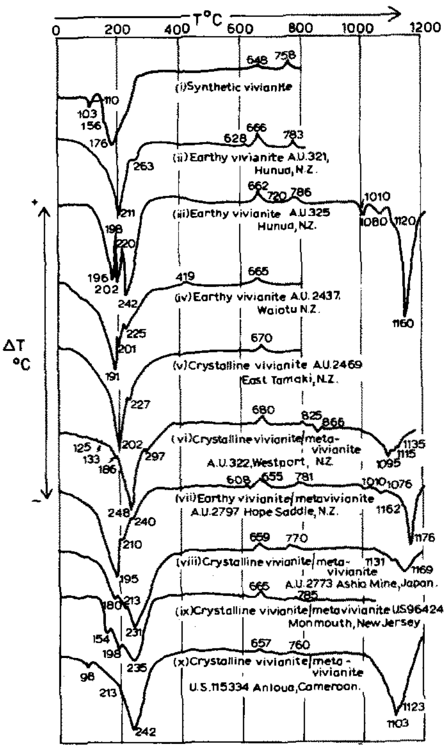

Fig. 1. DTA curves for synthetic vivianite, vivianite and vivianite/metavivianite admixtures from various localities.

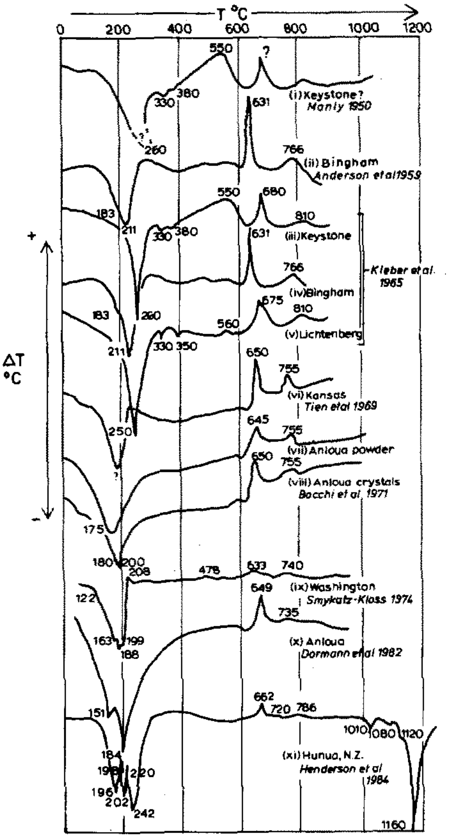

Fig. 2. DTA curves from existing studies of "vivianite". Adjustments have been made to reduce the published curves to a single, linear temperature and ΔT scale.

déshydratation et donc à la superposition d'une réaction exothermique et d'une réaction endothermique, tandis que la structure du minéral se detruit" (p. 156). In other words, there are no endothermic subpeaks per se representing expulsion of different groups of water molecules from the structure, but rather the pen returns towards the zero of the record when the output from the exothermic oxidation exceeds the differential output from the endothermic dehydration. The result is an exothermic peak described on the large endothermal peak and not an apparent bifurcation of the endothermic record as a result of some staged reduction in the differential endothermic output.

A distinct, fairly sharp, exothermic event which peaks between 657 and 670°C is recorded for all specimens, with some showing a smaller exotherm between 622 and 628°C. It was found that on the whole, peak temperatures were reproducible for any one sample and in both cases there was little or no baseline drift. Both Manly [1] and Anderson et al. [2] regarded this event as reflecting oxidation of the Fe^{2+} but this is now known to occur over a wide temperature range and to be largely complete by this stage of the analysis [3,5,7,8]. Rather, the peak shape is typical of that found in thermally induced physical changes such as structural transformations where a transition front is set up and propagates rapidly through the sample [20].

A similar but smaller and broader exotherm is recorded in many samples between 775 and 787°C. Interpretation of this and the earlier exotherm are often linked. For example, Kleber et al. [3] and Tien and Waugh [4] regarded the two peaks as arising from a phase change and reversible polymorphic transition(s), while Bocchi et al. [5] gave X-ray evidence that simultaneous, irreversible recrystallisation of two ferric phosphates occurred followed by a phase change.

Both infrared and X-ray diffraction examinations of quenched samples of the previously formed amorphous product show that from about 450°C ferri-phosphate phases start to appear but these become only significant following the 660°C exothermal event. Low-quartz type α-$FePO_4$ is the dominant phase with a minor amount of cubic $Fe(PO_3)_3$. In the phosphate bands of the infrared spectrum, $\nu_3(F_2)$ vibrations can be detected as low as 300°C. These gradually coalesce as the temperature increases such that, following the 660°C event, they form a broad, symmetrical absorption band in the 1080–1020 cm^{-1} range. Similarly, O–P–O bending, ν_2, is first noted at about 450°C, by which stage distinct lines have appeared in the X-ray diffraction pattern, and by 660°C pronounced absorptions at 400 and 430–440 cm^{-1} are evident due to this activity. Bands develop at 700, 640 and 590 cm^{-1} in the same gradual way, and while these might be assigned to ν_4 phosphate vibrations they may also be due in part to Fe–O stretching. Bands reported in similar studies by Kleber et al. [3] at 950 and 1200 cm^{-1} were not detected.

Not all the lines found in the X-ray patterns can be assigned with confidence to the phases mentioned above. Nor are the results consistent between samples. For example, the phase $Fe(PO_3)_3$ often forms early. The lines of its X-ray signature are weak and tend to be diffuse. They usually weaken as the temperature increases past 660°C. The X-ray record of Bocchi et al. [5] obtained using high temperature diffraction equipment, shows similar results and while they interpreted these using the now obsolete ASTM powder diffraction data cards 3-0379 and 17-0837, the majority of their lines may be assigned to the low quartz type pattern of $FePO_4$ (29-0715) or $Fe(PO_3)_3$ (19-0638). A distinct line is recorded by them at 2.70 Å above 696°C. The same line is noted in some of the patterns obtained in the present study at various temperatures. Often it weakens and finally disappears at higher temperatures. Occasionally it reappears, as would seem to be the case in the record of Bocchi et al. ASTM diffraction data card

3-0379 also records the same line for a sample of strengite heated to 950°C. Here it is regarded as reflecting the metastable formation of small amounts of haematite (Fe_2O_3) in the heated product.

The evidence of the infrared and X-ray diffraction studies of the various quenched products are taken as indicating a gradual sintering of the amorphous material culminating in a sharp exothermic reaction involving structural ordering at 660°C. A similar reaction has been observed in the thermal record of zeolites following thermally induced destruction of the lattice [11].

The nature of the 780°C exothermic event is less clear but may be similar to that at 660°C as far as present results are concerned. X-ray patterns obtained by Bocchi et al. [5] suggest a new phase has appeared after this event. Similar results were obtained by Henderson et al. [8] but their interpretations were made using the older, now obsolete, ASTM diffraction data cards. A new, quartz-like phase appears in the present patterns, but not immediately following the 780°C event. Rather, its appearance is delayed until 800°C is reached, before which its signature is rather diffuse and weak. The change appears sluggish and is not complete until 1060°C. It is accompanied by a waning in the intensity of any $Fe(PO_3)_3$ lines that may be present in the pattern while the low quartz α-$FePO_4$ pattern persists until melting occurs. The new diffraction lines show a poor match with those given for high quartz type β-$FePO_4$ by ASTM diffraction data card 31-0647. Those recorded by Bocchi et al. show no match with this card.

These last named authors attempt to relate the various thermal products and events found at moderate and high temperatures to the phase diagram Fe_2O_3–P_2O_5 of Wentrup [21]. Although α-$FePO_4$ is an important phase between 600 and 770°C in both the diagram and the DTA product, this is the only similarity between the two. The phase diagram is that for a static, equilibrium experimental situation. The DTA record is dynamically derived while phases are found that lie outside the appropriate compositional/temperature ranges of the diagram which point to the thermal analysis being a non-equilibrium situation.

A broad complex endothermic event occurs between 1000 and 1200°C and represents complete decomposition and melting of all the ferric phosphate structures.

METAVIVIANITE

The only previous thermal study of metavivianite is that of Dormann et al. [7]. The results obtained in the present study are shown in Fig. 3(iii) and, in the absence of sufficient material to investigate the nature of the various products at different stages of the heating process, little can be added to the interpretations of Dormann and his colleagues.

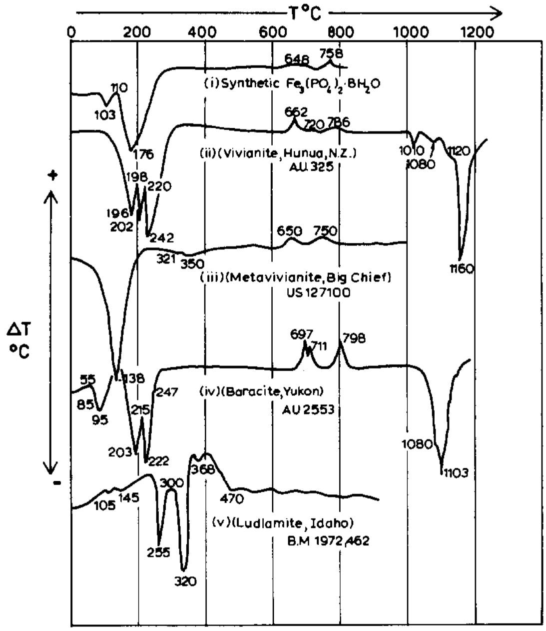

Fig. 3. DTA curves of synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$, vivianite (sensu stricto), type metavivianite, baraćite and ludlamite.

The two points which they stress as serving to distinguish the thermal response of metavivianite from vivianite are as follows.

(i) The simple nature of the initial endothermic event. The lack of any subpeaks and shoulders on the main curve is related to the fact that a large proportion of the iron in the sample is already oxidised and the signal from the endothermic dehydration is not interfered with by that from oxidation. In the present case a small shoulder occurred early on the endotherm, presumably reflecting the greater proportion of ferrous iron in this sample [19].

(ii) The presence of a second, binary endothermic event at between 320 and 365°C which is interpreted as representing dehydroxylation of the metavivianite structure. Again, in the present case, these peaks appear to be much smaller than those shown by Dormann et al. and may be reflect the smaller proportion of hydroxyl ions as a consequence of the lower degree of oxidation.

BARAĆITE

The differential thermal response of baraćite in air is shown in Fig. 3(iv) and can be seen to be very similar to that of vivianite as would be expected from the isostructural, solid–solution relationship between the two minerals [10,16]. In this sample of baraćite 55% of the cations are Mg^{2+}.

The broad endotherm from 55 to 150°C has already been discussed as probably representing loss of absorbed water. The major endotherm inflects at 150°C and shows two prominent subpeaks at 203 and 222°C with a small shoulder at 247°C. While recalling the earlier proviso, the total event as recorded is attributed to the endothermal loss of the structural water, exothermal oxidation of Fe^{2+} and consequential breakdown of the original structure.

Three distinct exothermic events are recorded, peaking at 697, 711 and 798°C. By analogy with vivianite, two of these responses may reflect a sintering reaction involving iron phosphate but may also involve a subsequent phase change. However, the third may result from formation of a high-temperature magnesium pyrophosphate lattice as reported by Roy et al. [22] in an analogous situation, while Manly [1] has noted a small exothermic peak in the record of $MgHPO_4 \cdot 3H_2O$ at 680°C.

Decomposition/melting of at least the iron phosphate portion of the charge is indicated by a complex series of endothermic reactions near 1100°C as in vivianite. Whether the resulting melt serves as a flux to aid fusion of the more refractory magnesium phosphate [9,23], or whether this compound or a modification persists as a solid above 1100°C could not be determined with the apparatus available.

Sturman and Mandarino [16] reported two differential thermal responses for baraćite: an endotherm at 220°C and an exotherm at 705°C, accompanied by a simple one-stage weight loss curve; no diagram was given. The absence of a record from 798°C and the singularity of the events at 220 and 705°C, may be attributed to differences in experimental techniques from those used in the present study.

LUDLAMITE

The pattern given by the differential thermal response of ludlamite in air is given in Fig. 3(v), and while it shows some broad similarities to that of vivianite, distinct differences are apparent which are believed to reflect directly the crystal chemical relationships that exist between the two mineral species.

As already mentioned, the initial broad endotherm is assigned to the loss of absorbed moisture. The corresponding TGA response stabilised before 150°C.

The major dehydration event inflects at 230°C and shows two, sharp, well defined, strong peaks at 255 and 320°C. However, the interpretation here is also that as given for vivianite and the real peak is the exotherm with a maxima near 300°C described on the large endotherm. The marked difference in the relative sizes of the exothermic and endothermic peaks of ludlamite compared with vivianite is believed to reflect the relatively greater proportion of Fe^{2+} being oxidised compared with the amount of water being expelled. This effect is enhanced by the higher reaction temperatures at which the dehydration and oxidation occur in ludlamite which is a direct result of the water molecules in ludlamite being shared between parallel bands of octahedra [24] in contrast with vivianite where the bands are linked by hydrogen bonds [25]. The more abrupt, steeper-sided nature of the ludlamite endotherm compared with the somewhat broader, cone-shaped vivianite endotherm is regarded as a direct reflection of the difference in bond type.

The total weight loss over this endotherm corresponds to approximately 2.5 molecules of water. Complete oxidation of iron would give a weight gain of $1.33H_2O$ and it appears from a comparison of the TGA and DTA traces that oxidation is apparently incomplete by the time the dehydration reactions are finished. Between 370 and 430°C a slight weight gain is recorded which appears to represent the completion of the oxidation. No distinct response is seen in the DTA curve which corresponds to this weight gain, nor would it be expected if, as in vivianite, the oxidation process is spread over a wide temperature range [3,7]. The validity of such an interpretation might well be explored with the type of magnometric titration used by Kleber et al. [3]. However, the present study does suggest that the kinetics of the oxidation of ludlamite are such that equilibrium was not approximated under the comparatively rapid heating conditions ($10° \ min^{-1}$) that were used.

Sluggish reactions also appear to effect the thermal behaviour of the mineral above 500°C. No distinct exothermal response was observed in the DTA curve such as might have been expected by analogy with vivianite. X-ray diffraction examination of the thermal decomposition products shows that a complete breakdown of the ludlamite structure follows the initial dehydration endotherm. Subsequently, the X-ray signatures of $Fe(PO_3)_3$ and low-quartz type α-$FePO_4$ are seen to develop in the thermal products; the intensity of the lines gradually increasing from 580°C. No lines of the high quartz type modification were found in any of the quenched products up to temperatures of 900°C.

VIVIANITE/METAVIVIANITE ADMIXTURES

In all samples studied, vivianite is the main phase present. Comparison of the records shown in Fig. 1 for vivianite and for vivianite/metavivianite admixtures show that the proportion of metavivianite in any sample is insufficient to show either of the distinctive characters of its thermal response in the curves of the mixed samples. A run made early in the study of a synthetic, microcrystalline $Fe_3(PO_4)_2 \cdot 8H_2O$ sample which had been left in the laboratory and had oxidised over a period of some weeks, showed a small but distinct endothermic peak at 294°C akin to that shown in Fig. 1 by the vivianite/metavivianite sample from Westport, New Zealand. This response may be from a dehydroxylation, and while it, or a similar response was recorded in a few of the patterns of other admixtures, it is lacking from the records of the last four curves of Fig. 1.

It can perhaps be noted that in the infrared spectra of many samples, of varying degrees of oxidation, that absorptions were found in bands characteristic of water such as 3400 and 1635 cm^{-1} in the heated products following the major dehydration. The absorptions were extremely weak but persist in samples up to 850°C, where the 1635 cm^{-1} band is no longer seen but some activity is still present in the region of 3400 cm^{-1}. It would seem that protonated oxygen atoms persist in the heated product and, as this occurred in both heated vivianites and the admixtures, the appearance of any secondary endotherms above the major endothermal event, should not be taken as indicating the presence of the metavivianite lattice in the original sample.

Dormann et al. [7] assigned the differences between the published thermal records of vivianites such as those of Manly [1] and Kleber et al. [3] to their having analysed "des cristaux oxydés, vraisemblablement composés de vivianite et métavivianite associées" (p. 157). This is not necessarily so. Some descriptions of the analysed samples leave little doubt that a proportion of metavivianite was probably present, but the results given here show that not only is there little difference between the thermal responses of vivianite and vivianite/metavivianite admixtures but there is considerable variation in response between samples that are monomineralic vivianite. This has occurred when numerous factors that can influence the output have been standardised, e.g., sample arrangement, thermocouples, heating rate, reference material, grain size and packing density, amount of sample and sample preparation. These factors alone could account for the apparently disparate results obtained by different workers (Fig. 2) without needing to consider the possibility of inhomogeneity of the samples studied. In this respect, Bocchi et al. [5] show that particle size can influence the results. Certainly, in the present study there appears to be a tendency of the initial major thermal response to occur over a lower temperature range among the earthy (cryptocrystalline) samples than for those consisting of crystal fragments reduced to a standard particle size; the standard size being coarser than that of the individual microcrystals of the earthy habit [8]. Conclusive results tend to be obscured by the interference of the oxidation reaction.

"The diversity of DTA equipment in use does not permit immediate comparisons of the results in different laboratories because DTA curves and data are influenced by many equipment factors" Smykatz-Kloss [11,p.3]. Insufficient is known about the conditions under which the differing runs of Fig. 2 were made to profer any judgement on the matter.

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