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Correspondence

The thermochemical behaviour of vivianite and vivianite/metavivianite admixtures from Borne (Netherlands) and Mangualde (Portugal)

Comment

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Introduction

Over fifteen, somewhat inconclusive studies of the thermal decomposition of vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, and related minerals have been reported. Two recent descriptions include those of Figueirodo et al. (1984), concerned with the thermal behaviour of vivianite from Mangualde (Portugal), and Riezebos & Rappol (1987), describing the mineral from Borne (The Netherlands). These two accounts were not included in a review by Rodgers & Henderson (1986) who also presented additional data from various world occurrences. The Portuguese and Dutch reports serve to amplify several points raised by Rodgers & Henderson and appear particularly pertinent when placed alongside earlier studies such as those of Vochten et al. (1979).

Instrumental and experimental considerations

Three major factors need to be recognised before any worth-while discussion of thermal results can be undertaken:

In the absence of suitable international standards, direct comparison of results between different laboratories is well nigh impossible. Equipment variations are a major source of apparently disparate results (Smykatz-Kloss, 1974). This point needs to be emphasised and re-emphasised. It would appear to be overlooked frequently in discussion of the thermal behaviour of minerals. Rodgers & Henderson (1986 pp. 10–11) regarded it as a primary factor in apparent inconsistencies between published thermal analysis curves of vivianite.

Of equal importance is the question of differences in experimental technique and procedure which can produce distinctly different thermal responses between identical samples – even when all instrumental factors have been standardised (e.g. Bocchi et al., 1971). It is essential in reporting results that details such as sample size, particle size range, packing, preparation, heating rates, dilution, atmosphere, nature and amount of reference are all clearly stated. While Riezebos & Rappol (1987) provide these, Figueiredo et al. (1984) do not, rendering their excellent account of less value than if they had. The differences in experimental conditions between Rodgers & Henderson (1986) and Riezebos & Rappol (1986) are shown in Table 1.

Thirdly, is the question of sample homogeneity. While this is always of importance in any thermal study, it is of particular concern in examining iron phosphates. Monoclinic vivianite readily oxidises, at least partially, to triclinic metavivianite. The two are not polymorphs despite some similarities of lattice and formulae (Poullen, 1979; Dormann et al., 1982; Rodgers, 1986) and the two show subtly different thermal behaviour (Dormann et al., 1982; Rodgers & Henderson, 1986). Assuming any vagaries of instrumental response and sample preparation are eliminated, it is sometimes possible to detect the dehydroxylation of the metavivianite lattice in the presence of vivianite. Dormann et al. (1982) would ascribe the differences between results such as those given by Manly (1950) and those of Kleber et al. (1965) to different ratios of vivianite and metavivianite in their samples, as a consequence of these having experienced different degrees of oxidation.

Variability between samples from a single outcrop and even between grains and fragments of grains from a single vivianite specimen has been demonstrated by Dormann et al. (1982), Fejdi et al. (1980) and Rodgers & Henderson (1986). As such, considerable care needs to be taken in selecting material for thermal analysis and to ensure that any other data cited for vivianite from the locality concerned is directly relevant to the thermally analysed portion. In this connection, Figueiredo et al. (1984) give the analysis of Correia Nevis (1966) to provide a formula for the Mangualde vivianite. This shows Fe^{3+} as 38% of total iron or close to the 40% limit at which the monoclinic vivianite lattice totally collapses (Dormann & Poullen, 1980.) This contrasts, however, with Mössbauer results from another sample of the same vivianite which show only 8% Fe^{3+}. Any interpretation of the differential thermal and thermo-gravimetric curves of this vivianite must depend on whether a probable monomineralic sample or a mixture of two related substances have been analysed. No X-ray data obtained at ambient temperatures is provided relevant to the thermally analysed portion.

Riezebos & Rappol's (1987) X-ray results are perplexing, particularly in the light of the extensive data provided by Sameshima et al. (1985). The Borne vivianite shows an X-ray signature which contains additional lines over that of synthetic $Fe_3(PO_4)_2 \cdot 8H_2O$. Some may correspond to metavivianite reflections at 3.60, 3.06/3.01, 2.80 and 1.63Å. However, the strong 010 metavivianite reflection at 8.6Å is absent, as is that at 4.27 and an anomalous line at c.6.95Å which sometimes occurs in the pattern of oxidised vivianites (e.g. Minato et al., 1956). Unfortunately, no Fe^{2+}/Fe^{3+} ratios are given for the Borne samples.

Thermal results

Rodgers & Henderson (1986) reported most vivianite samples, as well as vivianite/metavivianite admixtures, as showing a strong endothermal event which inflects about 70°–110° C and attains a strong, apparent maximum near 190°–240° C. The record varies between samples while subpeaks and shoulders are frequently present on the sides of the record of the main event.

The Mangualde specimen conforms to this pattern but the Borne sample does not. The temperature maximum recorded for the Dutch vivianite is the lowest reported in the literature. Further, the curve shows subsidary shoulders and subpeaks near 120° and 182° C. Typically such inflections have been reported from higher temperatures (Rodgers & Henderson, 1986, Figs. 1 & 2). The low figures for Borne are very likely a reflection of the very fine grain size ($< 2\ \mu m$) of the sample. Bocchi et al. (1971) found that the maximum for this event

Table 1. Thermal analytical experimental procedures compared

	Rodgers & Henderson (1986)	Riezebos & Rappol (1987)
sample size	100/150 mg + 20 mg Al_2O_3	15 mg + 40 mg Al_2O_3
reference	100 mg Al_2O_3 annealed	60 mg Al_2O_3 annealed
grain size	100–200 μm	$< 2\ \mu m$
packing	loose, no tamping	tamped
heating rate	10° C/min	10° C/min
atmosphere	air, no turbulence	? air
crucibles	platinum 6 × 17 mm	platinum 10 × 35 mm
thermocouples	$Pt\text{-}Pt_{90}Rh_{10}$	

was 35° C lower for a powder of Anloua vivianite than that found for more coarsely crystalline material. Perhaps too, the tamping of the Borne powder by Riezebos & Rappol assisted in reducing the recorded temperatures by improving the thermal conduction between grains which is the primary means of dispersing energy within a sample at these temperatures.

The initial record is not that of a single thermal situation. More than dehydration is involved (Riezebos & Rappol, 1987). Current wisdom regards the record as an unstaged endothermal dehydration overwritten in part, by an unstaged exothermal oxidation (e.g. Bocchi et al., 1971; Dormann et al., 1982; Rodgers & Henderson, 1986). It is not a record of a staged waterloss pattern such as occurs in the dehydration records of chalcanthite and epsomite (e.g. Vochten et al., 1979).

Riezebos & Rappol (1987) draw attention to a broad bump in their DTA trace c.316° C. From the evidence of Rodgers & Henderson (1986) it would seem likely that at this point the sample would be largely oxidised and have lost over 25% by weight, although it is not necessarily anhydrous. Some base line drift is common in the thermal record following completion of the dominant thermal event, presumably as a result of change in the relative heat contents of the sample and reference before and after the major early events. Small inflections have frequently been recorded in this region e.g. Lichtenberg vivianite by Kleber et al. (1965), Washington vivianite by Smykatz-Kloss (1974), as well as in vivianite/metavivianite admixtures.

Dormann et al. (1982) found a small, broad endotherm between 320°–365° C in the record of metavivianite which they interpreted as recording the dehydroxylation of the structure. While this record is frequently imprecise, it can enable the presence of metavivianite to be confirmed in some, but not all, vivianite/metavivianite admixtures. This would seem a possible interpretation of a 350° C endotherm recorded by Vochten et al. (1979) from a Retie (Belgium) vivianite sample and may also explain the bump labelled '316' in the Borne record of Riezebos & Rappol (1987, Fig. 5). However, in view of the variations shown by the base line in their record, it is not possible to eliminate some instrumental response as the cause of this inflection.

Rodgers & Henderson (1986) also noted that samples appeared to be seldom fully dehydrated or dehydroxylated following heating to 400° C (and higher). Fig. 3 of Figueiredo et al. (1984) would appear to confirm this with weak absorptions characteristic of water remaining in the IR spectrum of a sample heated to 400° C.

The interpretation of the c.650° and 780° C exothermal events have been discussed at length by Rodgers & Henderson (1986). The sharpness and symmetry of the record of these events in both the Mangualde and Borne DTA curves is typical of that resulting from a thermally induced physical change where a transition front is set up and rapidly propagates through a sample (Daniels, 1973). Only following this event do ordered ferri-phosphate phases become significant in the degraded sample. Again, the IR spectra of variously heated Mangualde vivianite separates would appear to confirm this. In the spectrum taken at 600° C, the phosphate $\nu_3(F_2)$ and ν_2 bands lack the definition they acquire in samples subject to higher temperatures. However, a caveat must be applied to the applicability of the physical data provided by Figueiredo and co-workers for the interpretation of their DTA/TGA record.

To obtain a plentiful supply of various thermal products for X-ray, infra-red and Mössbauer analysis, Figueiredo et al. (1984) heated separate samples to 400°, 500°, 600° and 750° for half hour periods. The products they obtained from this, essentially static processing of the parent material are not necessarily the same as those produced by the dynamic, non-equilibrium thermal analysis of the same vivianite. Results of comparison of samples treated by both techniques at the University of Auckland indicate they are often not equivalent. To obtain material for X-ray and infrared study, Rodgers & Henderson (1986) heated vivianite samples under the same 10° C/min gradients to those obtaining in the analytical furnaces, followed by quenching the crucibles and contents once the required temperatures had been achieved.

Both the 650° and 780° C events are taken by Rodgers & Henderson as involving sudden structural ordering following a gradual sintering of earlier formed products. However, detailed evidence to support this contention was lacking in their own work as well as in the earlier study of Bocchi et al. (1971). In view of the above comments, the data of Figueiredo et al. (1984) do not help confirm this view.

Observations

The results of Figueiredo et al. (1984) and Riezebos & Rappol (1987) highlight the need for international standards to be employed in support of published thermal analytical results, particularly in view of the difficulties posed by equipment variations and differing experimental procedures which are peculiar to thermal analysis. Irrespective of whether such standards become available, these difficulties make it desirable that authors adopt a rigorous format in reporting thermal results, in order that their data be of maximum value. If editors and referees were to insist on this, so much the better. Smykatz-Kloss (1974) provided such a format, particularly as it pertains to minerals. Regretably, his recommendations have all too frequently been ignored. There would seem to be little point in reporting further DTA and TGA curves of vivianite or its relatives, unless detailed chemical and physical data are provided for the specific fragment which is being thermally analysed, along with standard curves of some substance such as potassium hydrogen phthalate to permit ready correlation with results from other laboratories.

Reply

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In view of several earlier publications dealing with iron phosphates (Rodgers, 1977; Henderson et al., 1983, 1984; Sameshima et al., 1985; Rodgers & Henderson, 1986), Rodgers may be regarded as an expert on the examination of the thermal behaviour of vivianite and related mineral phases. The insert of our Borne vivianite description in his comments may therefore be considered as a credit and is greatly appreciated.

Rodger's discussion of the Mangualde (Figueiredo, 1984) and Borne vivianites first of all affords us an opportunity to supplement the comparison of thermo-analytical procedures as presented in his Table 1: The Linseis L62 two channel recorder (Riezebos & Rappol, 1987) is also equipped with Pt – Pt_{90} Rh_{10} thermocouples, and the Borne vivianite was heated in a furnace atmosphere of air without currents or turbulence. Furthermore it gives a chance to enter a little more profoundly into the general character of the discussion.

To convey his comments Rodgers utilizes his dissatisfaction with the lack of international standards – and implicitly with the loose, inaccurate or incomplete way of communicating relevant data by authors – in reporting thermoanalytical results. He concludes his discussion suggesting that it is useless to report thermal curves of vivianite and related phases without detailed chemical and physical data of the thermally analysed sample.

We question whether such a gloomy conclusion is justified and are disposed to disagree with it.

Instrumental variations, differences in experimental technique and procedure, and sample heterogeneity are re-emphasized by Rodgers as the three major factors that render published thermal curves of iron phosphates hardly comparable, and therefore of less or no use to other workers in the field. It goes without saying that Rodgers is right in maintaining that by extensive and accurate mention of data and further special features concerning apparatus, technique and procedure, the situation would be improved. Also that information about chemical and physical data of the thermally analysed material – if available – would be essential for a better interpretation of the curves.

In a recent paper it has been shown that, even if the first two factors affecting the shape of DTA curves have been standardized, still a considerable variation in response upon dynamic heating of monomineralic vivianite samples may occur (Figs. I, II, III, IV Rodgers & Henderson, 1986). Thus, in spite of the application of the same equipment, techniques and procedure, thermal curves apparently may continue to reflect – in addition to the typical characteristics produced upon dynamic heating – a number of probably original and paragenetic properties as crystal-size, crystal-size distribution, crystal chemistry, etc. And the interaction of these two kinds of properties might be the cause of the different thermal responses as appears from the obtained curves. Therefore we think that samples that are for instance monomineralic according to their X-ray patterns, will not always yield equally shaped thermal curves. Or, to put it more generally, separate interpretations of the X-ray signature and of the thermal curve, both obtained from the same sample, do not always lead to an identical diagnosis as to the amount and nature of the composing mineral phases.

Since the work of Poullen (1979), Dormann & Poullen (1980) and Dormann et al. (1982) triclinic vivianite (metavivianite) may be regarded as a structural modification of the monoclinic phase. The reduction in structural symmetry is thought to be caused by progressing oxidation of Fe^{2+}, associated with a transformation of water molecules into hydroxyl groups. But the fact that monoclinic vivianite may act as a precursory phase of metavivianite, does not preclude the possibility of a more or less simultaneous origin of both, particularly in natural environments giving rise to very fine-grained aggregates (earthy vivianites). In response to changing Eh, pH and ion activities, they might also precipitate in succession within the same micro-environment. It can neither be precluded that an initial ratio vivianite/metavivianite is considerably changed post-depositionally by natural oxidation processes.

Among the users of DTA techniques two categories may be distinguished. The first one applies DTA as a means to describe extensively and in detail the dynamic thermal behaviour of a single or a mixture of related mineral species, in order to understand the curve characteristics and the positions on the curve of endo- or exothermic events. For this group of users it is of vital interest to know exactly which species are heated and, if several related ones are present, in which ratio they are occurring. The second category employes DTA as an (additional) identification method. Often the material to be identified is encountered as a minor component of samples, collected and sometimes partly treated for various objectives totally unconnected with the aim of the first category.

This second group of people cannot be compelled to collect more specific data for the convenience of the first group; after all they form the customers of that first category of scientists! Also it seems not wise to dissuade this clientele from reporting their data, how incomplete it might be from the viewpoint of the first group. For, in spite of a lot of environmental geochemical work done (Emerson, 1976; Emerson & Widner, 1978; Postma, 1981; Hearn et al., 1983 and further references cited in these articles), products and mechanisms of the interaction of iron and phosphorous under all possible natural circumstances are still incompletely clarified. True, geochemical constraints which define the conditions of formation of several hydrated iron phosphates have been formulated, but the sorts of natural environments in which they have been or are operative is probably still insufficiently known. And knowledge concerning the various possible geological occurrences is another interesting and indispensable aspect of the matter. Cutting off an information channel which might augment this knowledge, how defective the information about the exact nature of the solid phases might be, seems highly undesirable.

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