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Thermal stability of the soil minerals destinezite and diadochite $Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 6H_2O$ – Implications for soils in bush fires

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ABSTRACT

Thermogravimetry combined with evolved gas mass spectrometry has been used to ascertain the stability of the soil minerals destinezite and diadochite $Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 6H_2O$. These two minerals are identical except for their morphology. Diadochite is amorphous whereas destinezite is crystalline. Both minerals are found in soils. It is important to understand the stability of these minerals because soils are subject to bush fires especially in Australia. The thermal analysis patterns of the two minerals are similar but not identical. Subtle differences are observed in the DTG patterns. For destinezite, two DTG peaks are observed at 129 and 182 °C attributed to the loss of hydration water, whereas only a broad peak with maximum at 84 °C is observed for diadochite. Higher temperature mass losses at 685 °C for destinezite and 655 °C for diadochite, are due to sulphate decomposition, based upon the ion current curves. This research has shown that at low temperatures the minerals are stable but at high temperatures, as might be experienced in a severe bush fire, the minerals decompose.

1. Introduction

There are many minerals found in soils, many of which are formed from aqueous solutions. Some of the minerals remain as the so-called colloidal minerals [1–4]. Two such minerals are destinezite and diadochite $Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 6H_2O$. The name “destinezite” is given to samples that are triclinic and crystalline, while diadochite is poorly ordered and X-ray amorphous. Both minerals have the chemical composition: $Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 6H_2O$. The mineral destinezite is a hydrated hydroxy phosphate of ferric iron with some sulphate substitution, with the iron in the ferric state [3,5–7]. The mineral [6] is triclinic with cell parameters = 9.584 Å, $b = 9.748$ Å, $c = 7.338$ Å, $\alpha = 93.07^\circ$, $\beta = 95.78^\circ$, and $\gamma = 105.32^\circ$. According to Peacor et al. [6] the crystal structure consists of infinite chains of $Fe(O,OH,H_2O)_6$ octahedra, sulphate tetrahedra and phosphate tetrahedra linked by a unique system of vertex sharing. The chains are weakly bonded into layers by hydrogen bonding between OH and H_2O of the Fe(III) octahedra and oxygen ions of the sulphate tetrahedra [6]. Layers of tetrahedral/octahedral chains alternate with sheets of H_2O molecules. Peacor et al. [6] states that the structure resembles hydrated clay minerals, with H_2O molecules that act as hydrogen bond donors and acceptors to oxygen atoms of adjacent slabs. The mineral has a clay-like appearance under a scanning electron microscope (SEM). The amorphous form of the mineral is called diadochite and is commonly regarded as a colloidal mineral [1–4]. This no doubt defines why the composition of the mineral is open to question at least in terms of the number of waters of hydration. Indeed it is not known whether the two minerals are identical or not. The mineral is yellowish brown to reddish to brownish black and all colours in-between. The mineral may ion exchange with many cations and as a consequence the colour varies.

The mineral is diagenetically related to delvauxite $CaFe^{3+}{}_4(PO_4,SO_4)_2(OH)_8\cdot 4\text{-}6H_2O$, which is also amorphous or possibly triclinic [8–10]. These minerals are formed through the reaction of acid sulphate solutions with already formed phosphate minerals. Because of the known and ill-defined structure of these minerals, it is very important to undertake structural studies. Due to the amorphous nature of diadochite, the application of thermoanalytical techniques is very important. The minerals are found in soils and caves [6,11].

The minerals destinezite and diadochite act as a sink for both sulphur and phosphorus in soils. Further, the minerals have been found in old or ancient burial sites. There is a vital need to study the thermal stability of these minerals in more detail and to ascertain whether the minerals are stable in a bush fire environment. To the best of the authors’ knowledge no such studies have ever been undertaken.

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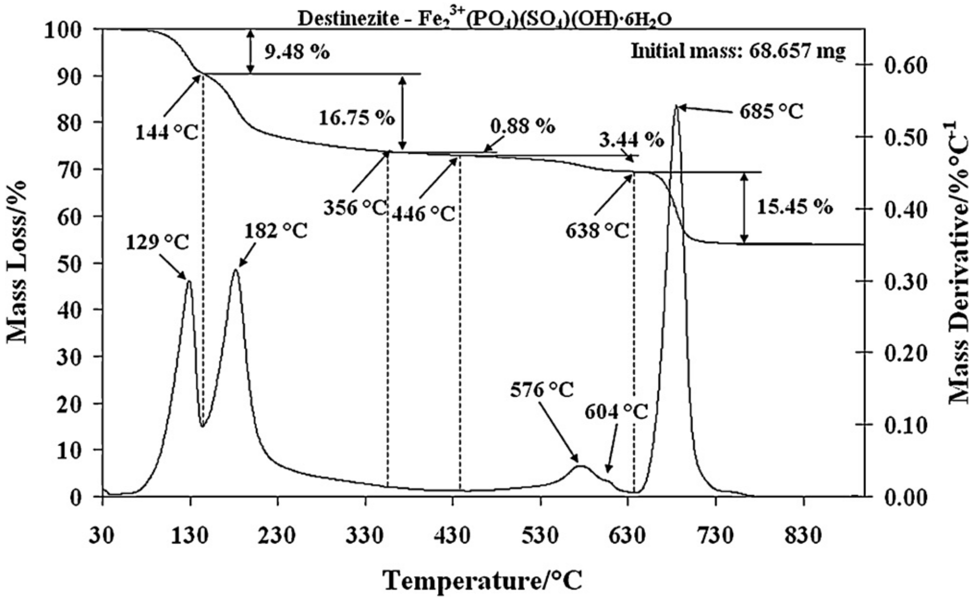

Fig. 1. Thermogravimetric analysis of destinezite.

2. Experimental

2.1. Minerals

The mineral destinezite originated from Argenteau, Visé, Liège Province, Belgium and was supplied by The Mineralogical Research Company as was the diadochite which originated from Alum Cave Bluff, Great Smoky Mts, Sevier Co., Tennessee, USA.

The minerals have been analysed and the data published [12].

2.2. Thermogravimetric analysis

Thermal decomposition of the destinezite and diadochite was carried out in a TA® Instrument incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 68 mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 1000 °C at high resolution. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water and sulphur dioxide were analysed. X-Ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu Kα radiation (1.54052 Å).

3. Results and discussion

The results of thermogravimetric analysis of destinezite and diadochite are displayed in Figs. 1 and 2, respectively. The ion current curves of the evolved gases of these two minerals are shown in Figs. 3 and 4. The DTG curve of destinezite displays mass loss steps at 129, 182, 576, 604 and 685 °C with 9.48, 16.75, 3.44 and 15.45% mass losses. For diadochite, three mass loss steps are observed in the DTG curve at 84, 124 (shoulder), 289, 655 °C, and 723 (shoulder) with

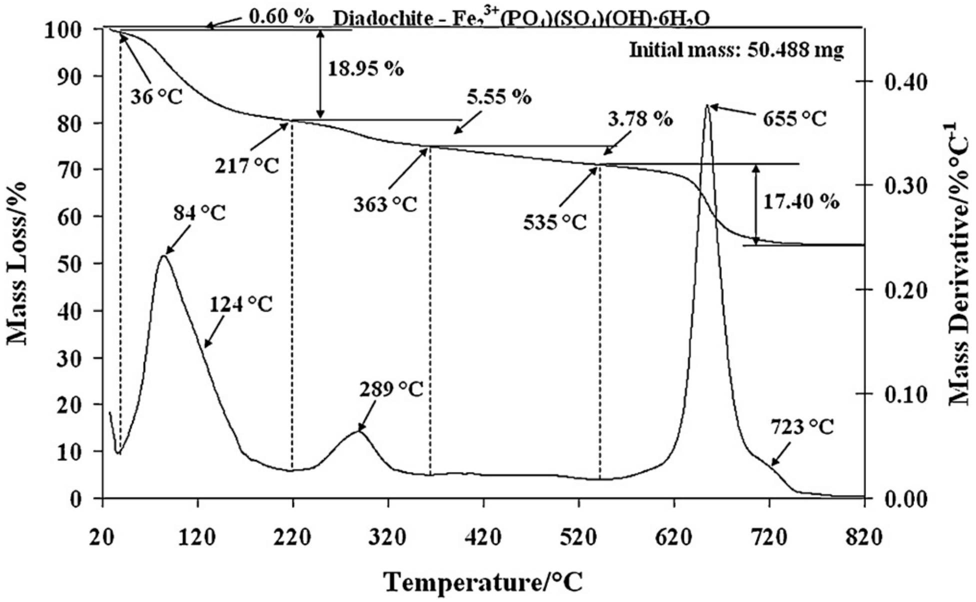

Fig. 2. Thermogravimetric analysis of diadochite.

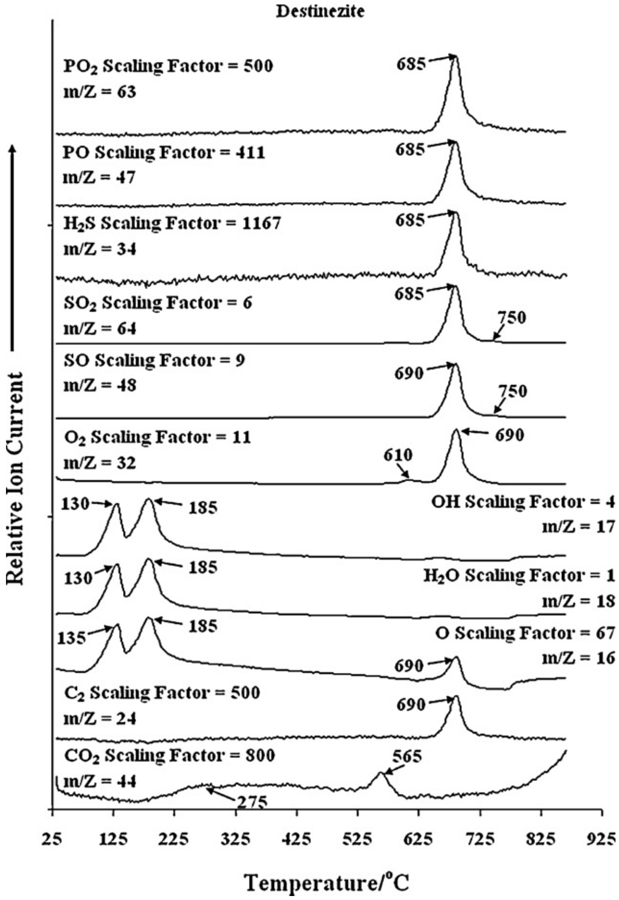

Fig. 3. Ion current curves of the evolved gases resulting from the thermal decomposition of destinezite.

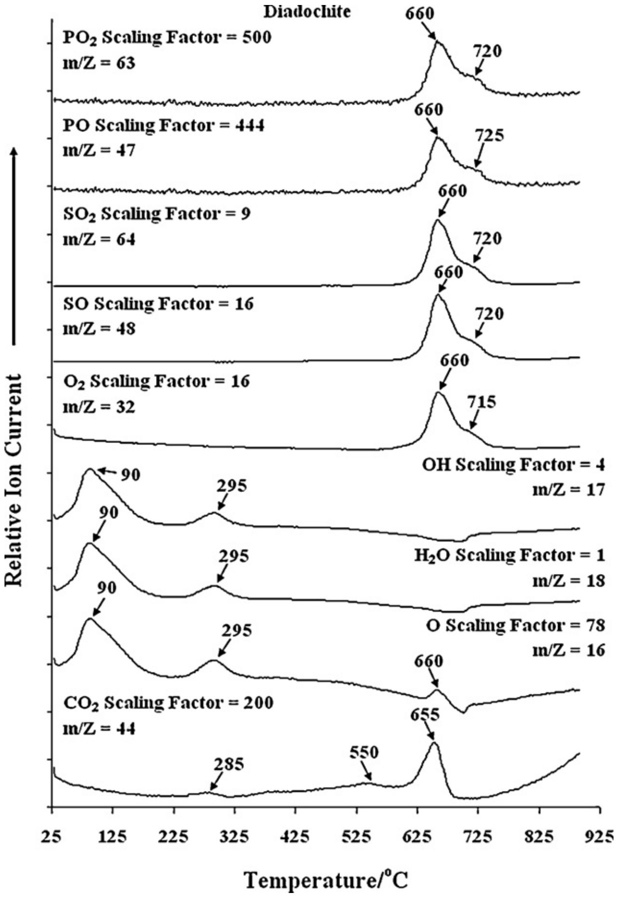

Fig. 4. Ion current curves of the evolved gases resulting from the thermal decomposition of diadochite.

mass losses of 18.95, 5.55 and 17.4%. There is a strong resemblance between the two thermal analysis patterns, which goes some way to confirm that the two minerals are closely related. Destinezite is the crystalline product of the diadochite gel. The crystallinity of destinezite appears to cause the dehydration of the structure to occur at more defined temperatures, compared to diadochite where broad peaks are observed.

Mass losses observed below 200 °C are attributed to the dehydration of the mineral structures. The mass loss at 189 °C is approximately double the mass loss observed at 129 °C. Therefore, the mass loss dehydration steps of destinezite are given by the following equations:

$$Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 6H_2O \rightarrow Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 4H_2O + 2H_2O \text{ at } 129\,^{\circ}C$$

$$Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 4H_2O \rightarrow Fe^{3+}{}_2(PO_4)(SO_4)(OH) + 4H_2O \text{ at } 182\,^{\circ}C$$

For diadochite, these two mass loss steps overlap, and the DTG maximum occurs at 84 °C. The DTG curve of diadochite is strongly asymmetric on the higher temperature side and a peak may be resolved at 123 °C. The maximum in the DTG curve at 84 °C is assigned to the loss of water from the diadochite gel. In addition, a mass loss of 5.55% is observed at 289 °C. The ion current curves show that water is the evolved gas at around this temperature (295 °C). The formula of destinezite contains OH units. It is probable that the mass loss at 182 °C is not only due to dehydration but also due to dehydroxylation. The following decomposition step is proposed:

$$2Fe^{3+}{}_2(PO_4)(SO_4)(OH) \rightarrow 2Fe^{3+}{}_4O(PO_4)(SO_4)_2 + H_2O$$

If the formula $Fe^{3+}{}_2(PO_4,SO_4)(OH)\cdot 6H_2O$ with 6 moles of water is used, the formula mass is 428 amu. The total loss of water is 25.2%. The total mass loss for destinezite at 129 and 182 °C is 26.23%, which is in harmony with the theoretical result. The total mass loss for diadochite is 24.9%, which again is close to the theoretical result. It is not clearly understood why there is a mass loss at 289 °C for diadochite, which is not observed for destinezite. However, it is proposed that the poor crystallinty of diadochite traps some water molecules in its disordered structure, which then requires additional energy (heat) to remove.

A mass loss step is found at 576 °C for destinezite. There are no maximums in the ion current curves for any of the expected evolved gases, except for a peak for $m/Z = 44$ at 565 °C which is attributed to CO_2 evolution. Thus, the 3.44% mass loss over the 530–630 °C temperature range is attributed to the presence of some carbonate impurity. These peaks are not found in the thermal analysis patterns of diadochite. This seems to support the concept that the colloidal mineral diadochite is purer than destinezite.

There is a high temperature mass loss for destinezite at 685 °C with a mass loss of 15.45%, while for diadochite a mass loss of 17.40% at 655 °C occurs. In the ion current curves for destinezite, maxima are observed for SO_2, PO_2 and related gases at 685 °C. The maximum for diadochite for SO_2 is 660 °C with a second maximum at 720 °C. There is a small shoulder observed at 725 °C observed in the DTG curves. The following reaction is proposed to occur:

$$Fe^{3+}{}_4O(PO_4)_2(SO_4)_2 \rightarrow Fe_3O_4 + 2FePO_4 + 2SO_3$$

4. Conclusions

The two minerals diadochite and destinezite have the same formula $Fe^{3+}{}_2(PO_4)(SO_4)(OH)\cdot 6H_2O$. Destinezite is the crystalline material, whereas diadochite has been described as a colloidal mineral and displays amorphicity. The question must be asked: are the two minerals identical. Such a question cannot be answered by XRD. Thermal analytical techniques go someway to showing some similarity in the two minerals. However, this is not definitive as the thermal analysis patterns of the two minerals show significant differences. Therefore, the question remains unanswered.

For destinezite, two DTG peaks are observed at 129 and 182 °C, and based upon the ion current curves are attributed to the loss of water of hydration. For diadochite, a broad peak at 84 °C is attributed to this water mass loss. The thermal analysis patterns of destinezite show small DTG peaks at 576 °C attributed to a carbonate impurity. The thermal analysis patterns of diadochite show an additional peak at 289 °C, which is assigned to the loss of water molecules trapped in the disordered structure. The higher temperature mass losses at 685 °C for destinezite and 655 °C for diadochite based upon the ion current curves are due to sulphate and phosphate decomposition. However, more sulphate anions are in the structures, illustrated by the smaller multiplicity numbers used in preparing the mass spectra.

What this work has shown is that the two stoichiometrically related minerals destinezite and diadochite are quite stable up to 200 °C. These minerals are found in soils and function as a phosphate and sulphate sink. The origin of relatively stable destinezite from diadochite gel-like medium in clayey parts of mineral dumps and similar media including soils, thus represents the possibility of phosphate/sulphate capture in the solid-solution phase and makes a sink for the free migration of phosphate into surroundings. The implication is that these minerals are stable even if exposed to bush fires.

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