

Identification by RAMAN Microscopy of magnesian vivianite formed from Fe^{2+} , Mg, Mn^{2+} and PO_4^{3-} in a Roman camp near fort Vechten, Utrecht, The Netherlands

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Abstract

The presence of a magnesian vivianite $(\text{Fe}^{2+})_{2.5}(\text{Mg}, \text{Mn}, \text{Ca})_{0.5}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, has been identified in a soil sample from a Roman camp near Fort Vechten, The Netherlands, using a combination of Raman microscopy and scanning electron microscopy. An unsubstituted vivianite and baričite were characterised for comparative reasons. The split phosphate-stretching mode is recognised around 1115, 1062 and 1015 cm^{-1} , while the corresponding bending modes are found around 591, 519, 471 and 422 cm^{-1} . The substitution of Mg and Mn for Fe^{2+} in the crystal structure causes a shift towards higher wavenumbers compared to pure vivianite. As shown by the baričite sample substitution causes a broadening of the bands. The observed broadening however is larger than can be explained by substitution alone. The low intensity of the water bands, especially in the OH-stretching region between 2700 and 3700 cm^{-1} indicates that the magnesian vivianite is partially dehydrated, which explains the much larger broadening than the observed broadening caused by substitution of Mg and Mn in vivianite and baričite.

Keywords: baričite, iron phosphate, Raman microscopy, vivianite

Introduction

The vivianite group forms a group of monoclinic phosphate and arsenate minerals with a general formula of $\text{A}^{2+}_3(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$, where X = P or As and A^{2+} = Co, Fe, Mg, Mn, Ni or Zn. Pure vivianite is the pure iron phosphate endmember. However solid solutions with other metals are often found, especially the incorporation of Mg. The mixed Fe/Mg equivalent is known as baričite. These minerals are often formed in acidic soils from peat bogs (Agsten, 1965; Postma, 1981), morasses and sediments (Rosenqvist, 1970; Shimada & Konno, 1971; Dell, 1973; Hearn et al., 1983; Henderson et al., 1984; Manning et al., 1991; Marincea et al., 1997), sometimes replacing organic material in for example fossil and recent animal and

human bones (Berg et al., 1967; Piepenbrink, 1989; Mann et al., 1998). In ground waters high in Mg and Fe it is possible that vivianite group minerals are formed due to the presence of phosphate from fertilisers used in farmlands or from sewage sludges (Frossard et al., 1997) or as chemical alteration product from guano (Anthony et al., 2000).

Spectroscopy analysis of the vivianite group minerals has been mainly limited to Fourier transform infrared spectroscopy (Omori & Seki, 1960; Sitzia, 1966; Hunt et al., 1972; Gevork'yan & Povarennykh, 1973; Hunt, 1977; Gevork'yan & Povarennykh, 1980). Only a very limited number of Raman studies of the vivianite group minerals have been published (Griffith, 1970; Piriou & Poullen, 1984; Melendres et al., 1989; Frost et al., 2002). Phosphate and arsenate

anions lend themselves very well for Raman spectroscopy and their tetrahedral anions in aqueous systems has been extensively studied (Ross, 1972). The symmetric stretching vibration of the phosphate anion (ν_1) is observed at 938 cm^{-1} , the asymmetric stretching mode (ν_3) at 1018 cm^{-1} . The ν_2 mode is observed at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} . Previous work on vivianite (Frost et al., 2002) has shown that the asymmetric stretching mode (ν_3) at 1018 cm^{-1} is split into three bands, while the symmetric stretching vibration (ν_1) is not split, corresponding with a reduced symmetry from T_d to C_s . These results were in good agreement with earlier work published by Piriou and Poullen (1984). The phosphate bending modes around 420 cm^{-1} also showed a split into two bands for vivianite and three bands for baričite and 567 cm^{-1} split into four and three bands respectively. The interpretation of the bands in this region is, however, not straightforward due to the complexity of this region.

In a soil sample provided by the Utrecht University Museum from an archeological Roman camp site near Fort Vechten near Utrecht, The Netherlands, a blue coloured material was observed that was tentatively identified as vivianite. Meeussen et al. (Meeussen et al., 1997) have shown that soil acidification and declining ground water tables have a significant influence on the decay of archeological remnants in acidic sandy soils. It is thought that in the specific case of the Roman camp at Fort Vechten that under the acidic conditions in the soil phosphate has been leached from materials present in the soil, such as waste, excrements and bone fragments, resulting in the neo-formation of vivianite. The iron and magnesium may have an anthropogenic origin (but not from bone) although a natural origin in the so-called gley-horizon in soils in the Dutch river areas is more likely (pers. comm. H. Kars). The formation of vivianite in the presence of iron together with other phosphates such as brushite and carbonates such as calcite from bone is not uncommon (Berg et al., 1967; Piepenbrink, 1989; Mann et al., 1998; Nakano et al., 1999). The release of phosphate and the presence of suitable bacteria or organic chelating and complexing molecules will result in the corrosion of steel and the formation of vivianite (Machu, 1973; Manning et al., 1980; Weimer et al., 1988; Bryant & Laishley, 1993; McNeil & McKay, 1994; Volkland et al., 2000).

Since the amount of vivianite was so small that it could not be identified by X-ray diffraction this study reports on an alternative, non-destructive method, Raman microscopy to identify these sorts of minerals in soils (Klopprogge et al., 1999).

Experimental

Sample origin

The soil sample was collected from a Roman camp at Fort Vechten near Utrecht, The Netherlands by the late Professor A. Wichmann (Utrecht University Museum sample G.104.1893). The vivianite single crystal was obtained from BK minerals suppliers and were large deep blue prismatic crystals. The mineral originated from the Ukraine, Russia. The baričite was obtained on loan from the South Australian museum sample number SAM 15065 and originated from Big Fish River-Rapid creek, Yukon, Canada.

Raman microscopy

The soil sample and the vivianite crystal were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting, function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX)

The vivianite samples were analysed for their morphology and chemical compositions using a JEOL JXA 840 electron probe micro-analyser with EDX attachment. Accelerating voltage was 15 kV and a take-

off angle of 40°. Moran Scientific software was used to control the EDS functions. Because the baričite sample was on loan from a museum no chemical analysis could be obtained in order to determine the exact amount of Mg and Mn²⁺ substitution of Fe²⁺.

Results and discussion

The soil sample consists mainly of a sandy soil rich in calcite and minor amounts of clay minerals. The presence of vivianite is indicated by the blue colouring of the soil after exposure to air, due to the oxidation of the iron in the vivianite structure. However, the amount of vivianite in the sample is too low to be detected by X-ray diffraction. The vivianite can be recognised as distinct crystals elongated along [100] in the SEM (Fig. 1).

The chemical analysis indicates that the vivianite has small amounts of Mg, Ca and Mn²⁺ substituted for the Fe²⁺ in its structure, no substitution of the phosphate anionic group has been found (Table 1). Most probably magnesium ions in the local groundwater acted as a source for the magnesium in the vivianite structure. The decomposition of the bone not only releases phosphate anions but also calcium cations, in addition to the fact that Holocene deposits

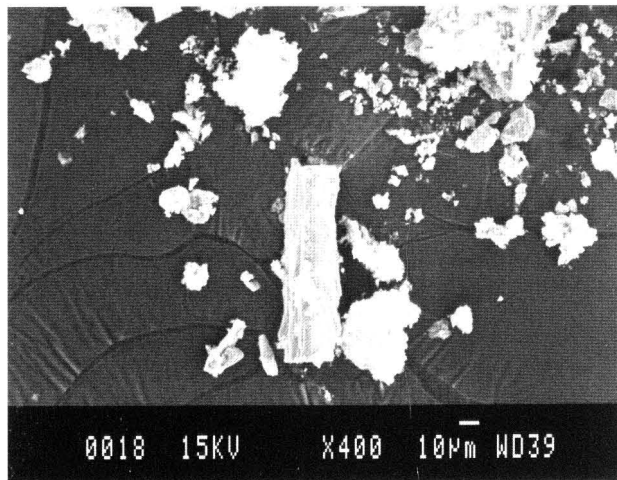


Fig. 1. SEM image of the soil sample with in the centre a single vivianite crystal.

Table 1. Chemical analysis of the soil vivianite.

Oxide	Weight %	
P ₂ O ₅	41.25 ± 0.35	2.00
FeO	51.33 ± 0.63	2.46
MnO	2.61 ± 0.13	0.13
CaO	0.75 ± 0.04	0.05
MgO	4.09 ± 0.16	0.35
Total	100.0	Cation sum 2.99

$\text{Fe}_{2.46}\text{Mn}_{0.13}\text{Mg}_{0.35}\text{Ca}_{0.05}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

of the Rhine are already carbonate rich, which explains the formation of relatively large calcite crystals in the sandy soil. Chemical analysis of the vivianite single crystal indicates that it only contains Fe²⁺, no substitutions are found for either the metal position or for the anion position. Because of the amount of Mg and Mn substituted in the soil vivianite a comparison is also made with another member of the vivianite group minerals named baričite (Mg,Fe²⁺)₃(PO₄)₂·8H₂O.

Fig. 2 compares the Raman spectra of the soil vivianite, a pure single crystal vivianite and baričite. A complete band component analysis is given in Table 2.

In general the spectra are in good agreement, although the bands in the soil sample are significantly broadened and shifted to higher wavenumbers. The blue colouring indicates partial oxidation of the soil vivianite sample but this only involves the outer atomic layers of the crystal and is not sufficient to cause any changes in the Raman spectrum. This is also supported by the chemical analysis where the metals to phosphate ratio indicates only very limited oxidation. Other possible explanations for the band broadening and minor shift are the substitution of Mg and Mn for Fe and the possibility of dehydration of vivianite minerals in soils when exposed to sunlight.

The comparison of the soil vivianite with pure vivianite and baričite indicates that due to the incorporation of a reasonable amount of Mg and a small amount of Mn and Ca the spectrum mostly resembles that of baričite. The substitution of Fe²⁺ by Mg and Mn in vivianite results in a minor shift to higher wavenumbers in baričite (Table 2), not only for the lattice modes but also for the phosphate bending and stretching modes. The broadening of the bands observed in baričite may be explained by the way the substitution takes place in the crystal structure. Since the crystal structure of vivianite and baričite are identical the Mg and Mn can only take the unique position of Fe in the lattice. Since in baričite the Fe/Mg ratio is mostly close to 1:1 (Sturman & Mandarino, 1976; Rodgers, 1987) it can not be determined from

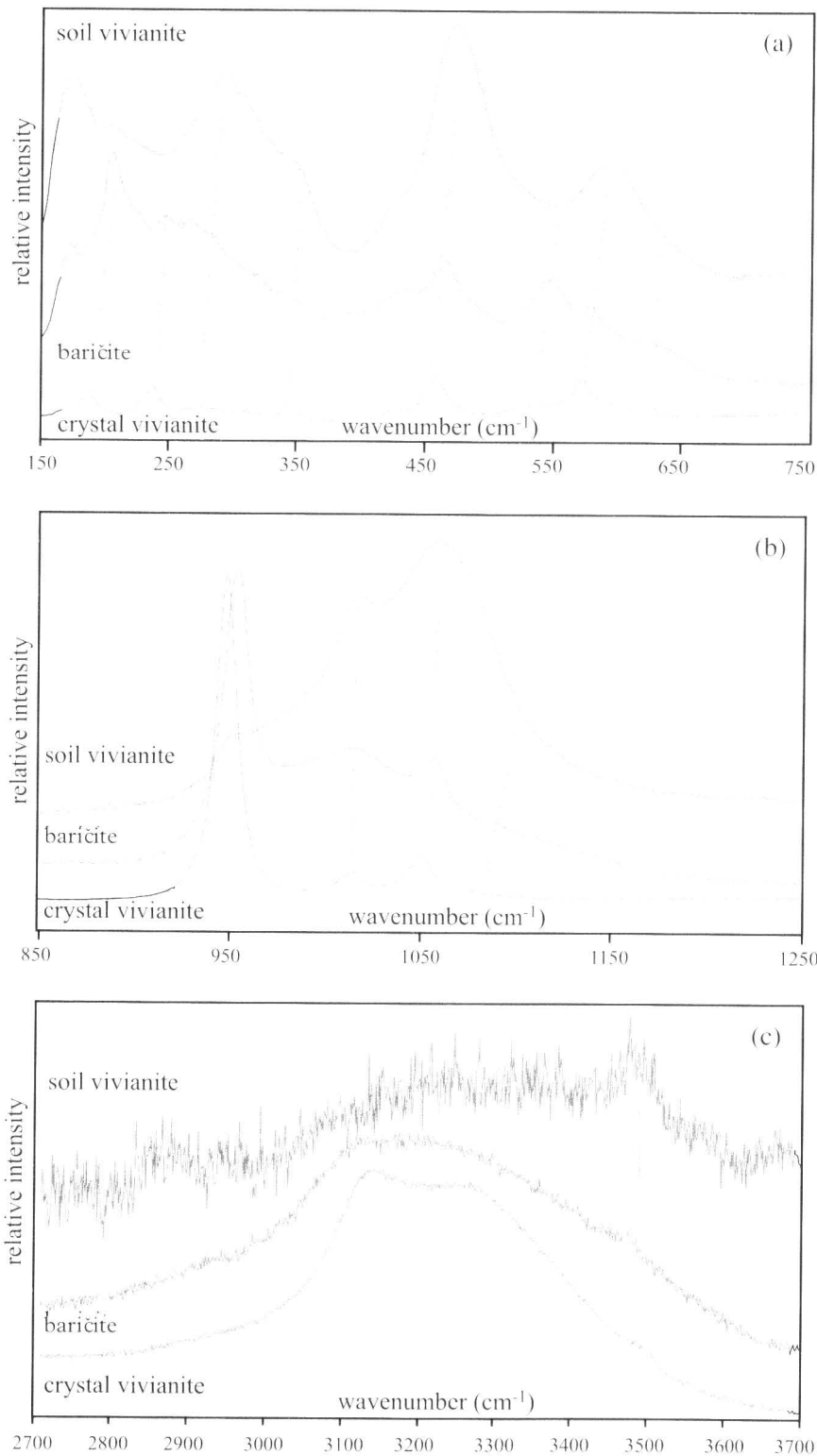


Fig 2. Raman spectra of soil vivianite, single crystal of pure vivianite and baričite in the regions (a) 150-750 cm⁻¹, (b) 850-1250 cm⁻¹ and (c) 2700-3700 cm⁻¹.

the spectroscopy whether the substitution is random or that segregation in different domains takes place similar to what happens in high-Mg calcite with a random distribution of Mg in comparison to dolomite where there are alternate layers of Mg and Ca separated by layers of carbonate (Deer et al., 1996). The scarce crystallographic information published for baričite indicates that it has a similar unit

cell and the same space group as vivianite, indicating random substitution (Sturman & Mandarino, 1976). The observed broadening can partly be explained by a random substitution of Fe in the soil vivianite by Mg and Mn. However, the broadening is too large to be ascribed to random substitution only since the broadening is significantly larger than that observed for baričite.

Table 2. Band component analysis of the soil vivianite Raman spectrum in comparison to baričite and vivianite.

Soil sample (cm ⁻¹)	Baričite ¹ (cm ⁻¹)	Single crystal vivianite ¹ (cm ⁻¹)	Assignment
3489	3480	3496	OH-stretching modes crystal water
3334	3300	3251	
3125	3121	3131	
2895	3025	3012	
1115		1081	P-O-stretching modes
1062	1057	1051	
1015	–	1015	
965	953	949	OH-libration modes crystal water
–	859	845	
765	–	–	Out-of-plane bending modes
591	572	572	
519	527	531	In-plane bending modes
471	461	456	
422	428	423	
346	340	342	Lattice modes
292	314	307	
	281	276	
222	212	236	
190	201	187	
169	170	166	

¹ (Frost et al., 2002).

Fig 2c shows the OH-stretching region with bands associated with the crystal water. Clearly the single crystal vivianite and baričite spectra are very similar. The soil vivianite spectrum, however, shows hardly any intensity in the OH-stretching bands except for the band around 3489 cm⁻¹. This is a clear indication that the sample is significantly dehydrated. Thermal analysis experiments (Frost et al., 2002) indicate that a large part of the dehydration takes place below 100 °C. Calculations have shown that from the 8 water molecules present 5 are lost in this low temperature reaction. Infrared emission spectroscopy in the hydroxyl-stretching region confirms the observation in the Raman spectrum, as the band around 3500 cm⁻¹ remains visible up to 400 °C. Partial loss of the crystal water will have a significant effect on especially the phosphate vibrations and to a lesser extent on the lattice vibrations. The removal of the water molecules from the crystal structure will result in an increase in stress and slight deformation of the crystal lattice without completely destroying the existing crystal structure. As a result the symmetric and asymmetric vibrations of the phosphate groups and the lattice vibrations will show a strong broadening, as is observed in the soil vivianite spectrum.

In conclusion, magnesian vivianite has formed from iron, magnesium and phosphate in the soil in a Roman camp. Due to the presence of Mg and Mn substituting for Fe²⁺ in the vivianite crystal structure a small shift and slight broadening is observed in the

Raman spectrum. Extra broadening is due to partial dehydration of the vivianite probably due to exposure of the soil to intense sunlight. This study shows that, Raman microscopy is a strong analytical technique that can help in the identification of these types of minerals without any sample preparation and without damaging the sample.

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