Geophys. J. Int. (2009) **177,** 941–948 doi: 10.1111/j.1365-246X.2009.04122.x

GJI Geomagnetism, rock magnetism and palaeomagnetism

Raman spectroscopy of iron oxides and (oxy)hydroxides at low laser power and possible applications in environmental magnetic studies

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Accepted 2009 January 15. Received 2008 December 19; in original form 2008 May 16

SUMMARY

Raman spectroscopy uses the inelastic scattering of electromagnetic radiation by molecules. Monochromatic light of a laser interacts with phonons, the vibrational modes in the crystal lattice. The energy of the scattered light is shifted by the scattering. The shifts in energy yield the Raman spectrum that is specific for each mineral because the phonons are specific for each mineral.

In this study, Raman spectroscopy of synthetic and natural iron (oxy)hydroxides and iron oxides was performed to test its potential in environmental magnetic studies and soil science. The main aim was to distinguish between the different iron oxides occurring in soils. Most of them can be identified by magnetic methods, but there are some minerals that are not easy to differentiate from each other. In these cases, the magnetic methods can be complemented by Raman spectroscopy. A major challenge is the fast transformation of many iron minerals if laser power is applied, especially if the material is poorly crystallized as often is the case in environmental material. In this study, very low laser powers were applied. Nevertheless, the investigated iron minerals could be distinguished from each other. Thus, a magnetic method to discern lepidocrocite and ferrihydrite in soil samples could be corroborated. It is also shown that Raman spectroscopy is an easy method to distinguish magnetite and maghemite. Due to the low laser powers applied, a wuestite band at about 595 cm^{-1} could be established enabling a non-ambiguous identification of this mineral by its Raman spectrum. Furthermore, the potential of the method to investigate magnetic material produced by soil bacteria is demonstrated.

Key words: Biogenic magnetic minerals; Environmental magnetism.

1 INTRODUCTION

Raman spectroscopy is a fast tool to distinguish iron oxides, hydroxides and oxyhydroxides. The method has been used for the analysis of corrosion products (Oh *et al.* 1998; Thibeau *et al.* 1978) or oxide scales formed in production processes (Bhattacharya *et al.* 2006), the characterization of pigments in archaeological material (Clark & Curri 1998; Damiani *et al.* 2003) and historical artwork (David *et al.* 2001), the determination of the mineral composition of meteorites (Rull *et al.* 2004) and the examination of small biomineralized material like chiton teeth (Lee *et al.* 1998).

Investigations of soil iron mineralogy by Raman spectroscopy have been scarce so far. However, the potential of the method is well demonstrated by the fact that Trolard *et al.* (1997) succeeded in giving evidence for the existence of green rust as a natural mineral in a soil. Soil iron minerals may be poorly crystallized, which leads to broadening of bands (Rull *et al.* 2004) or variation in the relative intensity of bands (de Faria *et al.* 1997), but not to a change in the position of the band. An influence of ion substitution on the spectra is probable (Rull *et al.* 2004).

A severe problem is the fact that some iron minerals are transformed easily when applying laser powers of 1 mW or more. Most of the iron (oxy)hydroxides are converted to haematite and, consequently, it is impossible to identify the original material. In some cases it will even remain unknown that a transformation took place.

In this study, the Raman spectra of several synthetic and natural iron minerals are measured. Different laser powers are applied to assess how susceptible to transformations the minerals are. The obtained spectra are compared with literature spectra, and recommendations are given as to which bands can be regarded as reliable identifiers, especially when applying low laser powers. Finally, some applications in environmental magnetic studies are proposed.

2 MATERIALS AND METHODS

Synthetic goethite and haematite were purchased from Bayer, Inc., Leverkusen, Germany (Bayferrox 910 and Bayferrox 120). Natural goethite and haematite are ochre samples from Rustrel in France. The two-line ferrihydrite is a natural sample taken from a stream bed at Col de Galibier (France). Six-line ferrihydrite was prepared by Stanjek & Weidler (1992). The lepidocrocite was produced as described by Schwertmann & Cornell (1991). The natural siderite sample was kindly provided by the institute of mineralogy of the

Ludwig-Maximilians University in Munich. Magnetite samples are standards used in the paleomagnetic laboratory of the University of Leoben. Apart from the magnetite samples, the same samples have been used in a thermomagnetic study of mineral transformations (Hanesch *et al.* 2006). A more thorough description of the samples and results of X-ray diffraction analyses can be found there.

Raman spectra were obtained with a Jobin Yvon LABRAM confocal-Raman spectrometer equipped with a Nd-YAG laser (100 mW, 532.2 nm) and diffraction gratings of 1800 grooves mm^{-1}. Detection is with a Peltier-cooled, slow-scan, CCD matrix detector. Laser focusing and sample viewing are performed through an Olympus BX 40 microscope fitted with a 100× objective lens. The spot size is *ca.* 6 μm, resolution is 2 cm^{-1}. Laser power can be reduced by filters to about 1, 0.1 and 0.01 mW.

The sample preparation is very easy. A small amount of the dry powder is placed on a glass slide. The spot that will be measured (diameter 6 μm) is determined by positioning the glass slide under the microscope. Most samples used in this study are homogeneous. However, due to the very small spot size, several spots on each sample were measured to avoid the measurement of a small impurity instead of the main mineral.

The spectrum can be observed during accumulation, which helps in adjusting the accumulation time. Here, a balance had to be found between quality of the spectrum and measurement time. At low laser powers, it is necessary to prolong the accumulation time.

Raman spectra are shown in this study without smoothing or line fitting to convey the original picture seen during the measurement. The only processing done was removing the spikes and calibrating frequency with the help of some standard materials (silicon, polyethylene and calcite).

3 RESULTS AND DISCUSSION

In the following subsections, the spectra of some minerals, measured in this study, will be displayed and compared to literature spectra. An overview of the bands measured for various iron minerals is for example given by Cornell & Schwertmann (2003). The bands that proved to be useful for the identification of the investigated minerals in this study are listed in Table 1.

3.1 Goethite

The Raman spectrum of the synthetic goethite measured in this study (Fig. 1) corresponds to the spectra of this mineral shown in the literature (e.g. Oh *et al.* 1998). The combination of a strong peak at 385 cm^{-1} with clear peaks at 244, 299, 480, 548 and 681 cm^{-1} is easy to distinguish from any other spectrum. Synthetic goethite was measured with a laser power of 0.1 mW.

Table 1. Bands that are defined as diagnostic for individual minerals.

Goethite	244	299	385	480	548	681
Haematite	225	245	290–300	412	–	–
Lepidocrocite	250	348	379	528	650	–
Siderite	184	287	731	1090	–	–
Ferrihydrite	370	510	710	–	-	–
Magnetite	310	540	670	–	–	–
Maghemite	350	512	665	730	–	–
Wuestite	595	–	–	–	–	–

Note: The list is based on the material measured during this study. The wavenumber of the most prominent band is underlined. Only the strongest bands may be visible at low laser powers (<0.1 mW), especially for two-line ferrihydrite and magnetite.

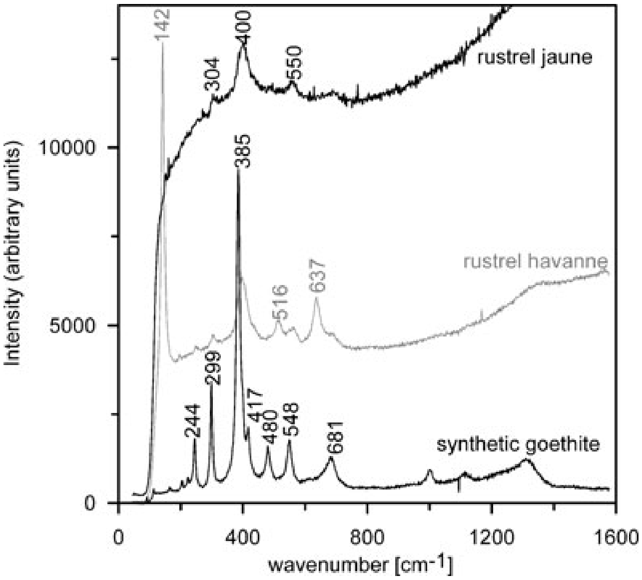

Figure 1. Raman spectra of goethite samples. Synthetic goethite shows the expected bands (measured at 0.1 mW, 2 min). The sample 'rustrel jaune' (yellow ochre) can only be measured at low laser power (0.01 mW, 20 min). The main bands of goethite are present, but weak and considerably broadened. Orange ochre (rustrel havanne) is more stable. It was measured with a laser power of 0.1 mW for 5 min. The same bands are visible as for the yellow ochre. Additionally, there are the bands of TiO_2 (anatase) at 142, 516 and 637 cm^{-1}.

The natural goethite samples are ochres from Rustrel in France: rustrel jaune and rustrel havanne. Rustrel jaune was destroyed by the laser beam even at a power of 0.1 mW; therefore, the ochre samples were measured at a very low power of 0.01 mW for 20 min (Fig. 1). The largest peak at 385 cm^{-1} merges with the peak at its flank (417 cm^{-1}) to a broad band around 400 cm^{-1}. The bands at approximately 300 and 550 cm^{-1} are weak and broadened. However, some other bands are lacking. Hence, the possibility cannot be excluded that the ochre may be a structurally different mineral rather than a poorly crystallized goethite. Clark & Curri (1998) proposed the formula $\mathrm{FeO}_{1+x}(\mathrm{OH})_{1-2x}$ for commercial yellow ochre. On the other hand, measurements of yellow ochres from archaeological studies may yield pure goethite spectra (Damiani *et al.* 2003), spectra as the one measured in this study (David *et al.* 2001) or spectra that correspond to a transition between the latter two (Clark & Curri 1998). These differences might well be caused by different crystallinities of the natural goethite found at different locations.

The example presented here shows that these natural pigments may be destroyed by rather low laser powers. Therefore, care should be taken when investigating archaeological specimens or artwork, which should not be altered.

Rustrel havanne is more stable than rustrel jaune. Its spectrum did not change when laser power was increased to 0.1 mW, but a further increase in power to 1 mW destroyed the sample. Rustrel havanne shows the same bands as rustrel jaune and additionally the bands of anatase, a form of TiO_2, at 142 and 516 cm^{-1}. The band expected for anatase at 394 cm^{-1} merges with the 400 cm^{-1} band of the yellow ochre.

3.2 Haematite

The synthetic haematite was also measured with low laser powers to test if the bands are visible under these conditions. Fig. 2 shows the

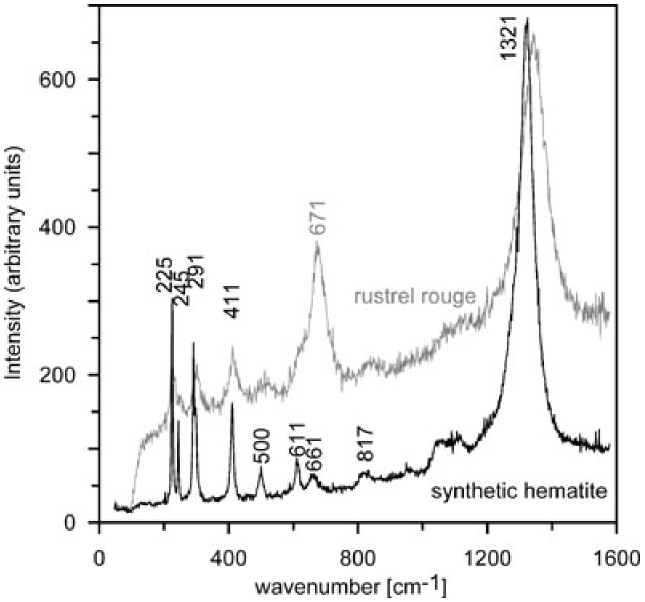

Figure 2. Raman spectra of haematite. In the spectrum of the synthetic sample the haematite bands are clearly visible although very low laser power was used (0.01 mW, 20 min). The additional bands between 600 and 1200 cm^{-1} might be caused by impurities. The spectrum of the natural haematite (rustrel rouge; 0.01 mW, 15 min) shows a maghemite band around 670 cm^{-1} in addition to the haematite bands.

result. The well-established haematite bands (e.g. Oh *et al.* 1998) are clearly visible at 225, 245, 291, 411, 500, 611 and 1321 cm^{-1}. The additional bands might be caused by impurities. The producer of this powder states that up to 4 per cent SiO_2 and Al_2O_3 may be present in the product. Olivine, for example, has bands around 820 cm^{-1}. Although iron oxides and hydroxides are poor light scatterers (de Faria *et al.* 1997), it is possible to characterize these powders reliably at low laser powers.

The natural haematite in this study is red ochre from Rustrel in France (rustrel rouge, Fig. 2). It clearly shows the haematite bands, albeit broadened in comparison to the synthetic sample due to the low crystallinity (Rull *et al.* 2004). An additional maghemite peak is visible at 671 cm^{-1}. The presence of maghemite in this sample was already shown by thermomagnetic measurements although it was not visible in the XRD pattern, possibly due to the very small grain size of 30–35 nm (Hanesch *et al.* 2006).

Measurement of the red ochre with a laser power of 0.1 mW led to non-identifiable and non-reproducible spectra after some minutes, which is a hint to mineral transformations. Red pigments in archaeological studies are usually identified as pure haematite (Damiani *et al.* 2003; David *et al.* 2001). There is the danger of transforming the maghemite, which is eventually present in red pigments, to haematite by higher laser powers.

The combination of bands, which is best used for the identification of haematite, is 225, 290–300 and 412 cm^{-1}. In most cases, the 245 cm^{-1} band is visible on the flank of the 225 cm^{-1} band.

3.3 Heated goethite

Heating of the synthetic goethite sample to 700 °C leads to the same spectrum as shown by the synthetic haematite sample (Fig. 2).

Heating the natural goethite samples (rustrel jaune and rustrel havanne) leads to a similar spectrum as measured for the natural haematite (rustrel rouge). The haematite bands are broadened, and a broad band between 670 and 690 cm^{-1} indicates the presence of maghemite. Colour of these samples is changed to red. The heated samples are further transformed at a laser power of 0.1 mW if it is applied for a longer time (more than 10 min). However, even at very low laser power (0.01 mW) a reasonably good spectrum was obtained after 10 min.

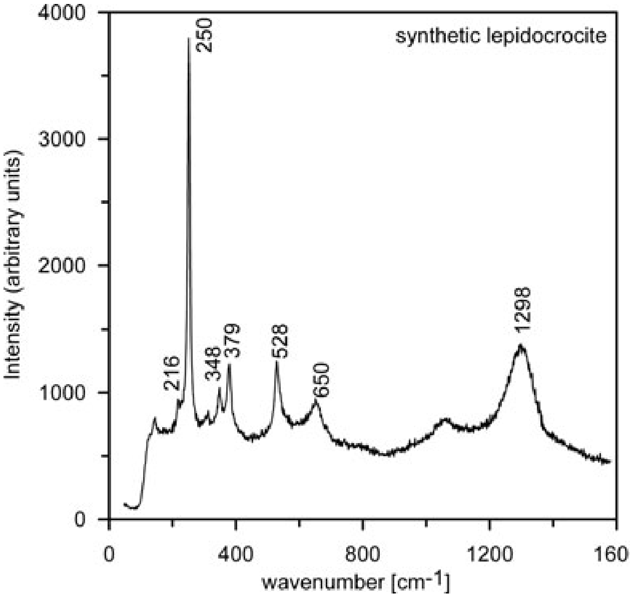

Figure 3. Raman spectrum of synthetic lepidocrocite (0.1 mW, 15 min). The spectrum agrees with the lepidocrocite spectra known from literature (e.g. Oh *et al.* 1998).

3.4 Lepidocrocite

The synthetic lepidocrocite (Fig. 3) yields the bands known from the literature (e.g. Oh *et al.* 1998): 250, 348, 379, 528, 650 cm^{-1}. It is stable also at 0.1 mW laser power. This mineral is especially interesting for the present study because maghemite is produced by heating the lepidocrocite to 400 °C (see Section 3.8).

3.5 Siderite

Siderite spectra are easy to obtain as the mineral is stable at moderate laser power. A spectrum measured with 1 mW is shown in Fig. 4. The bands coincide with published siderite bands (e.g. Rull *et al.* 2004) at 184, 287, 731 and 1090 cm^{-1}. Like in the case of lepidocrocite, the heated sample is especially interesting for this study. After the thermomagnetic measurement up to 700 °C the sample consisted of magnetite and wuestite as was shown by X-ray diffraction (Hanesch *et al.* 2006).

3.6 Ferrihydrite

Fig. 5 shows the Raman spectra of natural two-line and synthetic six-line ferrihydrite. The six-line ferrihydrite has three bands—370, 510 and 710 cm^{-1}—which are clearly seen in the spectrum measured at 0.1 mW. The same bands, albeit weaker, are seen at a laser power of 0.01 mW. At 1 mW, the spectrum changes. In the spectrum of the two-line ferrihydrite, only the strong 710 cm^{-1} band can be seen. This sample contains organic matter, which leads to fluorescence.

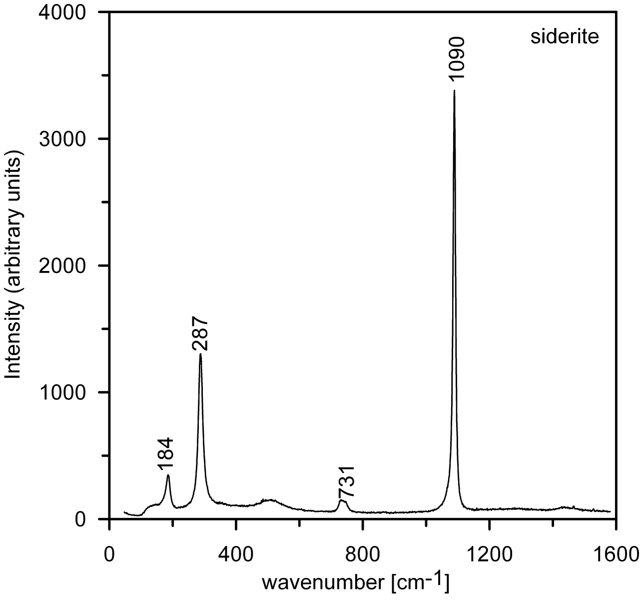

Figure 4. Raman spectrum of natural siderite (1 mW, 200 s). The siderite sample is not easily destroyed by the laser beam. A higher laser power can be used.

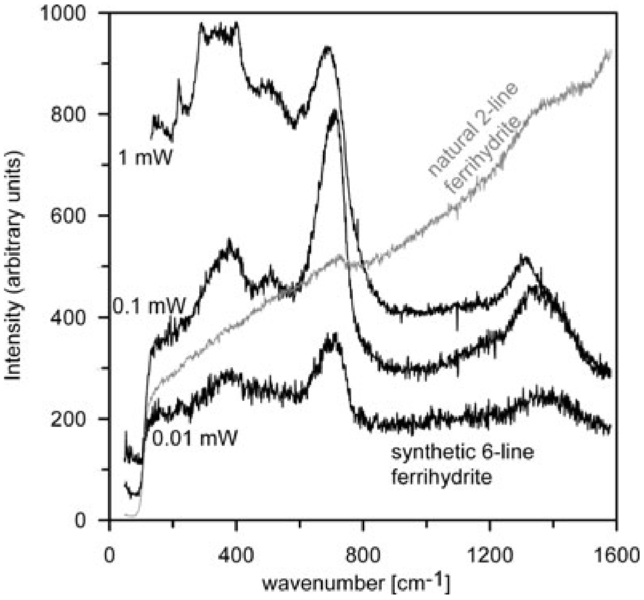

Figure 5. Three Raman spectra of six-line ferrihydrite, measured at different laser powers: 0.01 mW, 30 min; 0.1 mW, 15 min; 1 mW, 10 min. At the lowest power, the 510 cm^{-1} band is not discernible. At 1 mW, the spectrum starts to change because the mineral is transformed. The two-line sample contains organic matter, which leads to fluorescence. Only the band at 710 cm^{-1} is discernible (0.1 mW, 10 min). A similar, albeit weaker, spectrum can be produced at 0.01 mW with an integration time of 30 min.

Mazzetti & Thistlethwaite (2002) report that repeated scans and an increasing laser power led to the transformation to haematite for both forms of ferrihydrite. In the present study, a transformation of the samples was visible already at a laser power of 1 mW. After a longer exposure of the sample to the radiation, a haematite spectrum is measured. This is an example where a totally wrong spectrum can be identified if no care is taken about limiting laser power and time of exposure.

3.7 Magnetite

Magnetite is another mineral, which is prone to transformation if laser power is too high. This may be one of the reasons that the bands reported for magnetite are quite variable. de Faria *et al.* (1997) state three bands for magnetite: at 300, 532 and 661 cm^{-1}. Regarding their measurement at 0.7 mW laser power, however, only the band at 661 cm^{-1} is clearly discernible. It is the only band that is agreed upon by the literature, but its exact position varies between 661 cm^{-1} and 676 cm^{-1}. This variation might be caused by different laser wavelengths and powers used by different research groups. de Faria *et al.* (1997) compare the bands given by different workers, and it is conspicuous that those authors, who locate the band above 670 cm^{-1}, measure additional bands below 500 cm^{-1}. If these bands are explained by the occurrence of haematite, for example, due to transformation, it could be concluded that the shift to higher wavenumbers is caused by the onset of a transformation.

A second magnetite band between 532 and 550 cm^{-1} is agreed upon by almost all authors. An exception is Thibeau *et al.* (1978), who did not identify this band.

In this study, two magnetite powders were analysed, which are used as standard materials in the paleomagnetic laboratory. The two samples yield the same three magnetite bands at a laser power of 0.1 mW: at approximately 310, 540 and 670 cm^{-1} (Fig. 6). These three bands coincide with the measurement of the standard material by Rull *et al.* (2004) and Lee *et al.* (1998). At 0.01 mW, only the strongest band at 670 cm^{-1} is visible. The two powders used here had different surfaces. The one with the smooth surface was stable at 1 mW laser power. The powder with the rough surface started to transform at 1 mW. This agrees with the finding of de Faria *et al.* (1997) that crystals with a smooth surface are more stable. Shebanova & Lazor (2003) state that this laser induced oxidation differs from high temperature transformation due to photolytic and pyrolytic effects of the laser light.

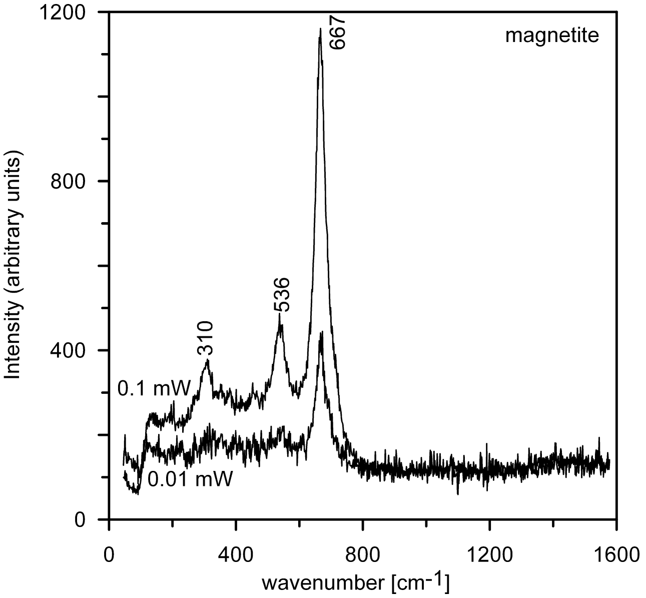

Figure 6. Raman spectra of magnetite produced by reduction of haematite. At 0.01 mW (25 min), magnetite can be identified only with the help of the 667 cm^{-1} band. At 0.1 mW (15 min), two additional bands are observed at 310 and 536 cm^{-1}. The sample transformed during the measurement with 1 mW laser power.

In mixtures of minerals, magnetite will usually be identified by the strongest band at 670 cm^{-1} because the others might be covered by the bands of other minerals. A more reliable identification can be done when all three bands are measured: 310, 540 and 670 cm^{-1}. As the band position is the same for all grain sizes, Raman spectroscopy cannot be used to determine the magnetic domain status of the material.

3.8 Maghemite

Maghemite was obtained by heating of the natural two-line ferrihydrite to 700 °C. X-ray diffraction showed that the sample consists mainly of maghemite with a small admixture of silica. 30 spectra of this sample were obtained with 0.01 mW. The laser power was kept low because 1 mW laser power led to the transformation of the maghemite to haematite and, hence, the measurement of haematite spectra. Two of the maghemite spectra are shown in Fig. 7. These two spectra contain all observed bands. Maghemite bands were identified at 350, 512, 664, 726 and 1330 cm^{-1} (black spectrum in Fig. 7). The bands coincide with those measured by Jacintho *et al.* (2007).

Small peaks of haematite are present in some spectra (224, 294 and 411 cm^{-1}). However, the 1330 cm^{-1} band is also seen when no other haematite bands are visible. This band is therefore not ranked as a diagnostic band. It appears for example in the grey spectrum in Fig. 7. In this spectrum, the 512 cm^{-1} band has shifted to 520 cm^{-1}, which might be caused by silica present. In other measured spectra, this silica band is much smaller and sharper.

The grey spectrum has a broadened band at 1360 cm^{-1} and an additional one around 1600 cm^{-1}. These two features are observed in several spectra and appear to be independent of the occurrence of maghemite, haematite or silica bands. They might be caused by burnt organic matter that should be present in the sample as carbon. Similar bands were for example measured by Kelemen & Fang (2001) in coal and by Tan *et al.* (2007) in graphite.

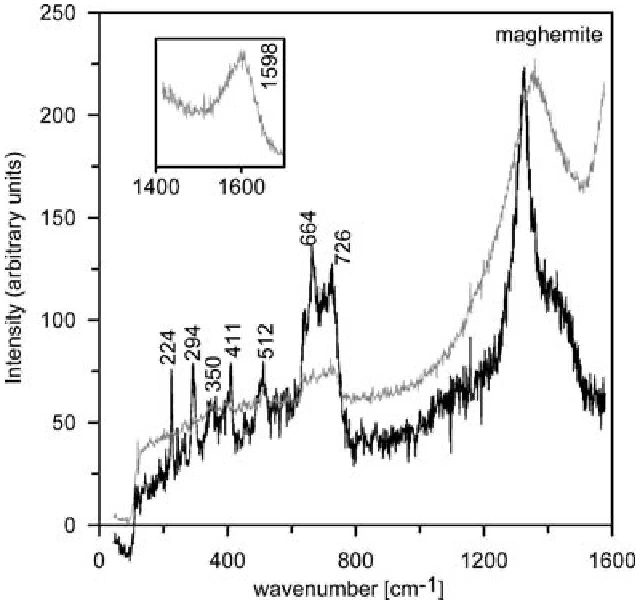

Figure 7. Raman spectra of maghemite produced by heating of natural ferrihydrite to 700 °C. One of the spectra (black, 0.01 mW, 5 min) shows small hematite peaks. The bands at 350, 512, 664, 726 and 1330 cm^{-1} are attributed to maghemite. The grey spectrum (0.01 mW, 20 min) was obtained at a different spot in the sample. Here, no haematite is present. The band above 1300 cm^{-1} is broader than for the black spectrum and an additional band exists at about 1600 cm^{-1}. This might point to the presence of burnt organic matter.

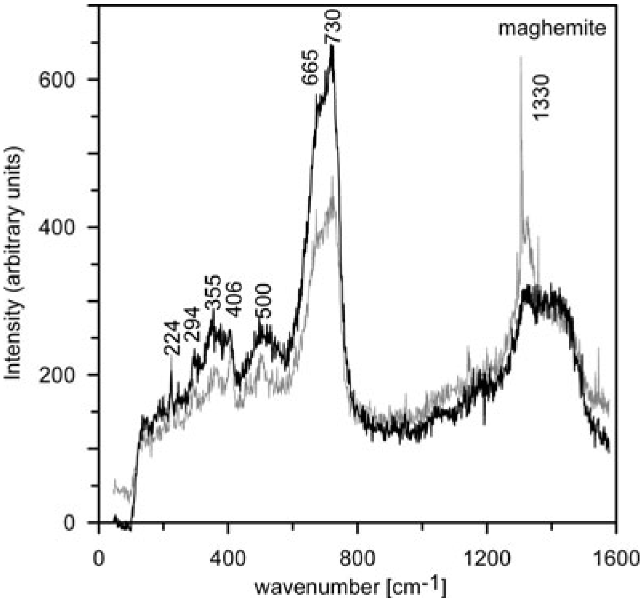

Figure 8. Raman spectra of maghemite produced by heating of lepidocrocite to 400°C. Again, some small haematite peaks are visible because part of the sample is oxidized. Grey line, 0.01 mW, 15 min; black line, 0.1 mW, 3 min.

de Faria *et al.* (1997) present a maghemite spectrum with three broad peaks at 350, 500 and 700 cm^{-1}. Two additional peaks at 1320 and 1560 cm^{-1} were not ranked as diagnostic by them, but they were used by Mazzetti & Thistlethwaite (2002) to identify maghemite during the transformation of ferrihydrite to haematite. In the present study, the two highest bands (1320 and 1560 cm^{-1}) occurred independently of the maghemite bands at approximately 350, 512, 665 and 730 cm^{-1}. They are therefore not regarded as reliable bands for the identification of maghemite.

This interpretation was confirmed by examining another maghemite sample. This sample was obtained by interrupting a thermomagnetic measurement of lepidocrocite at 400 °C. At this temperature, magnetization of the sample was highest (Hanesch *et al.* 2006) and lepidocrocite is known to transform via maghemite to haematite (Gendler *et al.* 2005). Spectra are similar when measured with 0.01 mW or 0.1 mW laser power (Fig. 8). Maghemite peaks are visible at 355, 500, 665 and 730 cm^{-1}. Part of the sample is further oxidized to haematite—either during the heating or by effect of the laser power. Measuring the sample with 1 mW laser power (2 min) yields the spectrum of pure haematite because the maghemite is transformed to haematite.

3.9 Wuestite

X-ray diffraction showed that the siderite had transformed to magnetite and wuestite after heating to 700 °C. Wuestite spectra shown in the literature (Thibeau *et al.* 1978; de Faria *et al.* 1997) look very similar to magnetite spectra, even when measured at laser powers below 1 mW. Therefore the suspicion arises that this mineral is transformed rather fast to magnetite and then further to haematite. The measurements in this study were started with 0.01 mW laser power and 5 min integration time. The 670 cm^{-1} band of magnetite is visible and an additional band at about 595 cm^{-1}. As X-ray

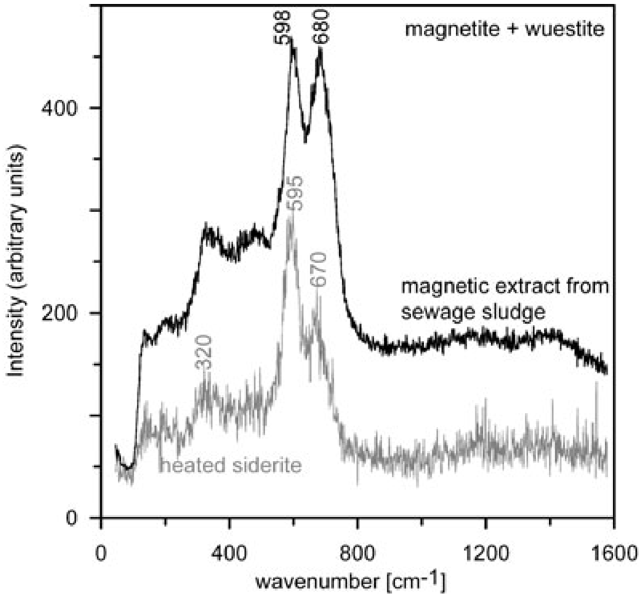

Figure 9. Raman spectra of samples containing magnetite and wuestite. Grey spectrum: siderite, heated to 700°C (0.01 mW, 5 min). The 595 cm^{-1} band is interpreted as a wuestite band. Longer integration time or higher laser power usually led to a change in the spectrum for this sample. Black spectrum: 'magnetite-shaped' particle in a magnetic extract from sewage sludge (1 mW, 5 min). This well crystallized particle is more stable in the laser beam than the heated siderite.

diffraction did not show the presence of other minerals, we conclude that this peak is indicative of wuestite. The sample showed an inhomogeneous behaviour. At some spots the same spectrum as shown in Fig. 9 was also measured with 1 mW laser power, but at most spots the spectrum started to change quickly with longer integration times and/or higher laser power. It is concluded that wuestite is easily converted and has to be measured with low power and short integration times, which may affect the quality of the obtained spectra.

To corroborate the assumption that the 595 cm^{-1} band is caused by wuestite, another wuestite sample was measured. It is an intergrown magnetite/wuestite crystal found in a magnetic extract of a sewage sludge sample (Gaisberger 2008). The peaks are similar to the heated siderite sample, but the intensity of the magnetite peak is higher relative to the wuestite peak (Fig. 9).

4 APPLICATION IN ENVIRONMENTAL STUDIES

4.1 Effect of H_2O_2 treatment on different iron oxides and oxyhydroxides

Recently, the identification of iron minerals in soils by thermomagnetic measurements was proposed (Hanesch *et al.* 2006). The method could well distinguish between goethite, haematite, magnetite/maghemite and ferrihydrite/lepidocrocite with the help of their different Curie temperatures or transformation temperatures. The main advantage of the method is the fact that the original soil sample can be measured without further preparation and even minute amounts of iron minerals can be identified. Only the distinction between ferrihydrite and lepidocrocite requires a further treatment of the sample. Both minerals have the same transformation temperature, but ferrihydrite reacts only in the presence of organic matter whereas lepidocrocite transforms also if it is present as pure mineral. It was therefore proposed to distinguish between ferrihydrite and lepidocrocite by treating the soil sample with H_2O_2 before the thermomagnetic measurement. There was some doubt, however, if the treatment with H_2O_2 would destroy some of the iron oxyhydroxides in the soil.

In the present study we tested the effect of the peroxide on the iron mineral powders. We took a small part of the samples and added 30 per cent H_2O_2 until the sample was totally covered. The samples where then dried at room temperature. This process took 3–5 d. After drying, the Raman spectra of the samples were measured. Exactly the same bands as before the treatment were measured for: synthetic goethite, natural goethite (rustrel jaune), lepidocrocite, synthetic haematite, natural haematite with maghemite (rustrel rouge), siderite, synthetic and natural ferrihydrite. When the second natural goethite sample, rustrel havanne, was treated with H_2O_2, it showed the same spectrum as rustrel jaune. Hence, the goethite was not affected by the treatment, but the additional TiO_2 phase we had found in this sample (Fig. 1; Section 3.1) was removed. It is concluded that the H_2O_2 treatment in combination with thermomagnetic measurements can be used to distinguish between goethite, lepidocrocite and ferrihydrite. Haematite and magnetite/maghemite can well be identified by magnetic methods (Maher *et al.* 1999). The distinction between magnetite and maghemite is treated in the next section.

4.2 Distinguishing magnetite and maghemite in magnetic extracts

Magnetite and maghemite behave similarly in almost all magnetic measurements. Maher *et al.* (1999) propose to distinguish these two minerals by analysing low temperature behaviour of susceptibility because magnetite shows the Verwey transition at 120 K. This method works well as long as the particles are large enough. Particles with superparamagnetic size do not display a Verwey transition (Goya *et al.* 2003), for example, paedogenic magnetic particles. Raman spectroscopy could be helpful in these cases if the magnetic phase is extracted before the measurement. The Raman spectra of magnetite and maghemite are sufficiently different. Magnetite shows bands at 310, 540 and 670 cm^{-1}, maghemite at 350, 500–515, 665, 730 and 1330 cm^{-1}. Although small particles may not show the bands below 650 cm^{-1}, these can be distinguished by the double peak of maghemite around 700 cm^{-1} and by the 1330 cm^{-1} band, which does not appear in magnetite.

In cases where magnetic measurements cannot distinguish between magnetite and maghemite, it would therefore be recommended to use Raman spectra, which are easy and fast to gain from magnetic extracts. Oxidized coatings of magnetite particles might be visible under the microscope. Care has to be taken in these cases because Raman measurements are spot measurements that only analyse the surface at a specific location and not the bulk of the sample as most magnetic measurements do.

4.3 Investigation of biomineralized material

Fig. 10 shows the Raman spectrum of the material that was magnetically separated from a bacterially enriched soil. The soil had been mixed with enrichment medium for anaerobic iron-reducing bacteria and poorly crystallized iron oxyhydroxides. The increase of magnetic susceptibility was then monitored for 200 d. The procedure is described in detail by Hanesch & Petersen (1999). Raman spectra were measured at 16 randomly distributed locations on the

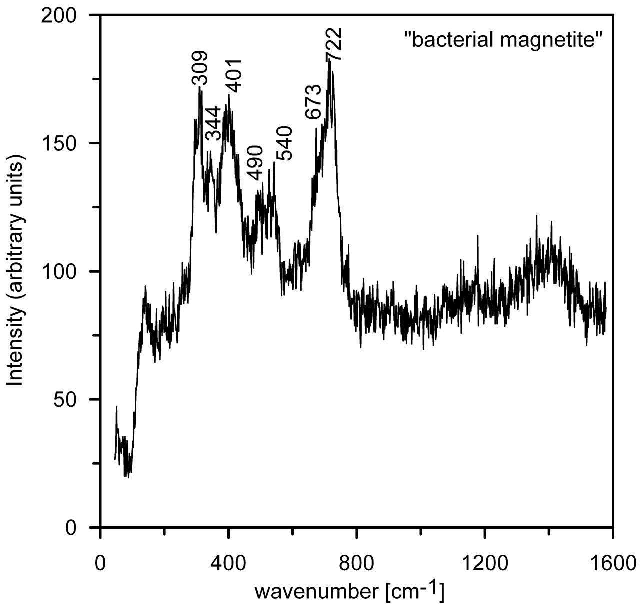

Figure 10. Raman spectrum of 'bacterial magnetite' (0.01 mW, 10 min). The sample shows magnetite and maghemite bands; hence a mixture of these minerals is present. Additionally, a band is visible at 403 cm^{-1} that points to poorly crystallized goethite (compare Fig. 1).

sample to avoid the results to be influenced by the operator, for example, by choosing only similarly looking locations. The spectrum was the same at all of these locations and also when measured with 0.1 mW. At 1 mW laser power, the bands start to shift.

The spectrum indicates a mixture of magnetite and maghemite. The broad band from 673 to 722 cm^{-1} is caused by both minerals. The maghemite band above 1300 cm^{-1} is relatively weak compared to the other bands, probably due to the presence of magnetite. Magnetite bands are observed at 309 and 540 cm^{-1}, maghemite peaks at 344 and 490 cm^{-1}. The band at 401 cm^{-1} resembles the one measured for poorly crystallized goethite in the natural ochres (Fig. 1). It will be caused by rests of the added iron oxyhydroxide mixture.

The bacterially enriched samples, which were used in this preliminary study, have been stored for some years. Therefore, it cannot be concluded that the bacteria produce both magnetite and maghemite. The sample may have been oxidized during the storage. However, these measurements demonstrate the potential of Raman spectroscopy for the characterization of pedogenically produced magnetic material.

5 CONCLUSIONS

5.1 Recommendations for the Raman measurements of natural iron minerals

Natural iron minerals are sometimes poorly crystallized and therefore transform rapidly during Raman measurements. Therefore, it is recommended that each measurement starts with the lowest possible laser power. In most cases, the dominant minerals can be identified also at very low laser powers (0.01 mW).

If a destruction of the sample can be accepted, higher laser powers may be applied to obtain high quality spectra and to find possible admixtures of other minerals. The same is valid if measurements at low power indicate only minerals that are known to be stable. However, as soon as new bands are identified, the possibility of transformations should be considered.

Figs 1–10 can be used to identify the different minerals. Comparing the figures is more useful than using tables of the bands because often the relative intensity of the various peaks helps during the interpretation of the spectra. The wavenumbers indicated in the figures should be regarded as approximate numbers as accuracy of the instrument may influence the measured wavenumber as well as the laser power applied. Poor crystallinity leads to a broadening of the bands.

5.2 Potential of Raman spectroscopy for studies in environmental magnetism

The main difference between Raman spectroscopy and most environmental magnetic methods is the size of the measured specimen. Whereas most magnetic measurements give information on characteristics of the bulk sample, Raman spectroscopy gives information on a spot of some micrometers. Hence, bulk measurements cannot be replaced by this method. For environmental samples, it will be necessary to separate the part of the sample that has to be investigated, for example, by magnetic separation like in this study or by gravity separation. Otherwise, the search for the components might be too time consuming.

Raman spectroscopy is especially promising if minerals are to be identified which display poorly defined XRD patterns (e.g. ferrihydrite) or which cannot easily be distinguished by other methods. The distinction between magnetite and maghemite will be the most interesting application for environmental magnetists. Raman spectroscopy yields a rapid result whereas the distinction may be hard to obtain by magnetic methods. Maghemite does not show the characteristic Verwey transition, but very small magnetite particles may not show it either. Although the magnetite band in the Raman spectrum seems to vary between 670 and 680 cm^{-1}, maghemite and magnetite can well be distinguished by the additional bands of maghemite at 720 and 1330 cm^{-1}. It is not clear if the variation of the magnetite band is caused by surface influences, grain size or even by partial oxidation.

A very promising application is the characterization of the magnetic material grown under the influence of bacteria. It could be shown in this study that the components of the 'bacterial magnetite' can well be identified. The small grain sizes of this material, however, require a very careful application of laser power.

ACKNOWLEDGMENTS

This study was financed by FWF grant V30-N19. The author would like to thank the staff of the Chair of Mineralogy and Petrology at the University of Leoben for the support during the Raman measurements. XRD analysis and interpretation was done by Helge Stanjek of the Institute of Mineralogy and Economic Geology, Aachen University. Two people kindly provided samples: Elisabeth Gaisberger, the sewage sludge samples; and Robert Scholger, (Paleomagnetic Laboratory Gams, University of Leoben) the magnetite powders. Many thanks to Barbara Maher and Cor Langereis for their helpful comments that lead to a much improved version of the manuscript.

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