Composition and genesis of rattlestones from Dutch soils as shown by Mössbauer spectroscopy, INAA and XRD

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Abstract

The chemical and mineralogical composition of rattlestones found near the main Dutch rivers has been studied by Mössbauer spectroscopy, INAA and XRD. Rattlestones are concretions of iron, formed in an environment of lateral iron accumulation, under the influence of periodical oxidation, around a fine core of ferruginous sediments, mainly clay and sand. The core has shrunk and detached itself from the mantle around it. ^{57}Fe Mössbauer spectroscopy was applied to identify the iron oxides, among which goethite is predominant. The goethite crystallinity was investigated by measuring its magnetic properties and its crystallinity, which is poorest at the outer side of the stone. The latter is confirmed by the broadening of the different X-ray reflections. In addition, illite and vermiculite were identified by XRD; these clay minerals were found mainly in the core.

The elemental composition was determined by INAA. The iron content in the mantle is about 50% by weight and gradually decreases outwards, while the core contains 2-15% Fe by weight. Differences between rattlestones from the Middle Pleistocene East of the Meuse river and those from the Late Pleistocene North of it are the absence of lepidocrocite and a richer mineralogy in the former.

It is concluded that the rattlestones are formed around a fine clayey core. Groundwater supplied the iron and other (trace) elements for the genesis. It is unlikely that rattlestones are the result of oxidation of siderite.

Keywords: crystallinity, goethite, iron accumulation, lepidocrocite, Mössbauer spectroscopy, rattlestones, siderite, trace elements

Introduction

Rattlestones have been known for long. They were referred to as 'aetites' or 'eagle stones' in Roman times (Adams, 1938; Bromehead, 1947). In spite of this, surprisingly little information is available on the chemical and mineralogical composition of these stones. Few previous publications dealt with rattlestones (Van der Burg, 1969) and with the climatological factors limiting their distribution in the Dutch Pleistocene (Van der Burg, 1971). The present contribution discusses the composition of several rattlestones found near the main rivers in the Netherlands, and their possible genesis.

According to a recent definition (Jackson, 1997), a rattlestone is a concretion composed of concentric laminae of different composition, in which the more soluble layers have been removed by solution, leaving a central part detached from the outer part, such as a concretion of iron oxide filled with loose sand that rattles on being shaken. Van der Burg (1969) suggested that rattlestones are formed by oxidation of siderite concretions which were deposited contemporaneously with the sediments in the beds where they are found today.

The geochemical and mineralogical characteristics of the rattlestones were investigated for the present study.

Material

Eleven rattlestones have been investigated. They were collected in several sand and gravel pits near the main Dutch rivers, i.e. at Koningsbosch East of the Meuse

river (Sterksel Formation, three specimens), and North of the Meuse at Deest, Lathum and Wapenveld (Kreftenheye Formation, four specimens) and at Leersum and Schaarsbergen (Drenthe Formation, four specimens). The codes used for these sites are Ko, De, La, Wa, Le and S, respectively; the Roman numbers I and II are used wherever necessary to distinguish between stones from one single site. An alterated siderite concretion found in the Reuver clay at about 30 m depth (Kiezeloöliet Formation) was studied, too, and coded Re.

The specific density of the stones was obtained by determining volume and weight. The latter varied between 30 and 500 g. The rattlestones were opened carefully in order to collect the loose, yellowish fine grains of the core, all of which weighed only a few percent of the stone. The specific density of the outer part of the stone (called 'mantle'), which was always less than 10 mm thick, was obtained and the size of the central cavity was determined.

Material from the core and several concentric laminae of the mantle of each rattlestone were powdered separately. The lamination is irregular and the laminae with a width of 1-2 mm frequently merge into one another (Van der Burg, 1969). Differences in hardness and color are helpful in making a separation between laminae. The interior material of the mantle is hardest and often also the darkest; the exterior material of the rattlestone is mostly quite soft and easy to scrape off the mantle. In total about 60 samples from the various rattlestones were investigated. Core samples are coded 1 and samples from the interior and exterior mantle material have been coded 2 and 3; in case more layers in the mantle are distinguishable, the consecutive layers have been numbered 2, 3 and 4. Material from different shells of the siderite concretion was sampled and numbered 1 (central segment), 2 (first shell), 3 (second one) and so on. In practice about 200 mg material per sample sufficed for detailed analysis. Munsell hues were used to determine the color of each sample (Cornell & Schwertmann, 1996).

Methods

The methods used for the investigation are nuclear techniques: Mössbauer spectroscopy (Kuzmann et al.,1998) and instrumental neutron-activation analysis (INAA), which were complemented by X-ray diffraction (XRD).

Mössbauer spectroscopy

Mössbauer spectroscopy is a very useful technique for investigating properties of Fe in soil iron oxides

(Coney, 1988). The structural order of iron oxides encountered in natural environments ranges from reasonably good to seemingly amorphous. This has a great influence on the magnetic properties. Deviations of the magnetic properties of iron oxides of very small particle size from those of coarse-grained counterparts lead to radical changes in their Mössbauer spectra (Van der Kraan & Van Loef, 1966; Murad, 1996). This is illustrated by the hyperfine field, which has a single value at any temperature in a pure magnetic crystal, but can vary greatly or even disappear at room temperature in a soil iron oxide like goethite. This type of spectroscopy can be used to distinguish between the two valence states of iron, e.g. in goethite and siderite, respectively.

Mössbauer spectroscopy is based on the recoil-free resonance absorption of gamma rays in certain atomic nuclei, for example the stable iron isotope ^{57}Fe (2% natural abundance). Gamma rays with an energy of 14.4 keV are emitted by radioactive ^{57}Co with a half-life of 270 days and the resonant absorption cross section of these (γ rays in ^{57}Fe is very high at room temperature. The method allows determination of nuclear energy levels to an extremely high accuracy, so that slight variations caused by different interactions between electrons and the nucleus become measurable. These interactions reflect differences in the electronic, magnetic, geometric or defect structure in solids. The spectroscopy is based upon the principle that, by moving the radioactive source, a very small energy shift can be attained in the emitted gamma rays, due to the Doppler effect.

The instrumental setup consists of the ^{57}Co-source, detector and the iron-containing sample in between; in such a transmission experiment, the Mössbauer spectrum (MS) obtained consists of the intensity of the (γ rays measured in the detector, plotted as a function of the source velocity. A minimum in MS corresponds with resonance absorption in the sample under investigation. A major value of Mössbauer spectroscopy as an analytical tool lies in the fact that any iron contained in a solid must show up in MS, independent of sample crystallinity or, of the form in which Fe is bound (Murad, 1988). Sample preparation is usually very simple; the sample thickness is about 50 mg/cm^2.

The distinction by Mössbauer spectroscopy of goethite, hematite, lepidocrocite and siderite is based on the magnetic hyperfine interaction. The first two oxides are magnetically ordered at room temperature and MS of both goethite and hematite consist of six-line spectra. The hyperfine field, B, in goethite at room temperature is known to be 38.5 T and that in hematite 51.5 T; the latter is used to calibrate the

source velocity in Mössbauer spectroscopy. The Mössbauer spectrum at 295 K (coded as MS[295K]) of paramagnetic lepidocrocite consists of two lines of equal intensity, the quadrupole splitting. The doublet is much larger in MS of siderite and readily distinguished from that of lepidocrocite. Speciation in a sample containing a few percent of Fe by weight is feasible. Poorly crystalline iron oxides can still be identified, in particular at lower temperatures. Spectral intensities of iron-containing species give information on their relative content in a sample. Further details on Mössbauer spectroscopy can be found in Kuzmann (1988).

Instrumental neutron-activation analysis

INAA is a quantitative method of high efficiency for the determination of a number of major and trace elements and supplies geochemical information on the material that may be involved in the formation and growth of rattlestones.

INAA has been applied at the nuclear reactor of IRI at Delft to determine major elements, in particular Fe, and many trace elements. The standard deviation and detection limit for Fe are less than 2% and about 100 ppm, respectively (Parry, 1991).

X-ray diffraction

XRD was performed to identify clay minerals. XRD patterns were obtained that enabled to determine peak positions and line widths of the iron oxides.

Diffractograms of about forty samples were made at the Laboratory of Soil Science and Geology of Wageningen University. The XRD was performed with a Philips PW 1710 diffractometer equipped with a graphite monochromator using CoK_α radiation. Peaks were recorded from 5° to 75° 2Θ. The clay minerals were thus identified, and the peak position and linewidth of the goethite reflections were determined.

Results

The cavities of the rattlestones vary widely and can take more than 50% by volume; this has a great effect on the specific density of the rattlestone as a whole, as shown in Figure 1. The horizontal bar indicates the density range of the numerous stones investigated by Van der Burg (1969), which only partly overlap with the densities of our rattlestones.

The other characteristics, as shown by MS, INAA, XRD, and those regarding the hue of the specimens, are dealt with in the following subsections.
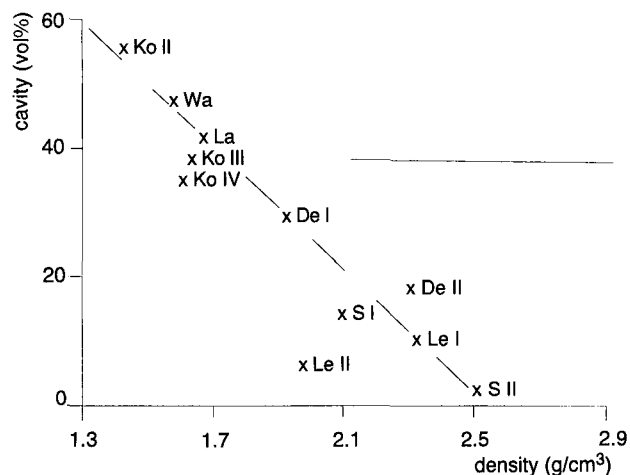

Fig.1. Cavity in the various rattlestones versus the density. The dashed line is drawn as a guide to the eye. The horizontal line indicates the range of densities of the stones investigated by Van der Burg (1969).

Mössbauer spectroscopic data

MS[295K] and MS[77K] of three samples from Ko II are shown in Figure 2. A central doublet dominates the spectra at 295 K and has practically disappeared at 77 K. A six-line magnetic hyperfine splitting attributed to goethite dominates MS[77K]. The doublet in MS[295K] is mainly due to goethite and to a limited extent to clay minerals. This follows from their relative intensities measured in MS[77K]. Remnants of a hyperfine splitting are still visible in the spectra of Ko II-1 and Ko II-2 at 295 K, but not in Ko II-3. The doublet resembles that of a paramagnet, but it is also characteristic of superparamagnetic goethite, due to extremely small crystallites. This is most pronounced in Ko II-3. In general, the sextets at 77K consist of asymmetrically broadened lines indicating a distribution of hyperfine fields due to a spread in goethite crystallite size. The smaller the size, the lower the hyperfine field (Van der Kraan, 1972). The distribution is narrowest in MS[77K] of Ko II-1 and widest in that of Ko II-3, while the hyperfine field is highest in the former and lowest in the latter (Table 1). Hence, the goethite crystallite size in the core is larger than in the exterior part of the mantle.

In MS[77K] of Ko II-1 and Ko II-3, the resonant absorption in the centre is attributed to non-magnetic minerals. It can be assigned to illite (XRD). Besides, a small signal is measured at a source velocity of about 3 mm/s that originates from an Fe^{2+} contribution; the accompanying line of the doublet is submerged in the central part of the spectrum. X-ray diffractograms confirm the assignments of goethite and illite. In the XRD of Ko II-1, illite is more pronounced than in Ko II-3 (see Table 2), which is contrary to the relative in-
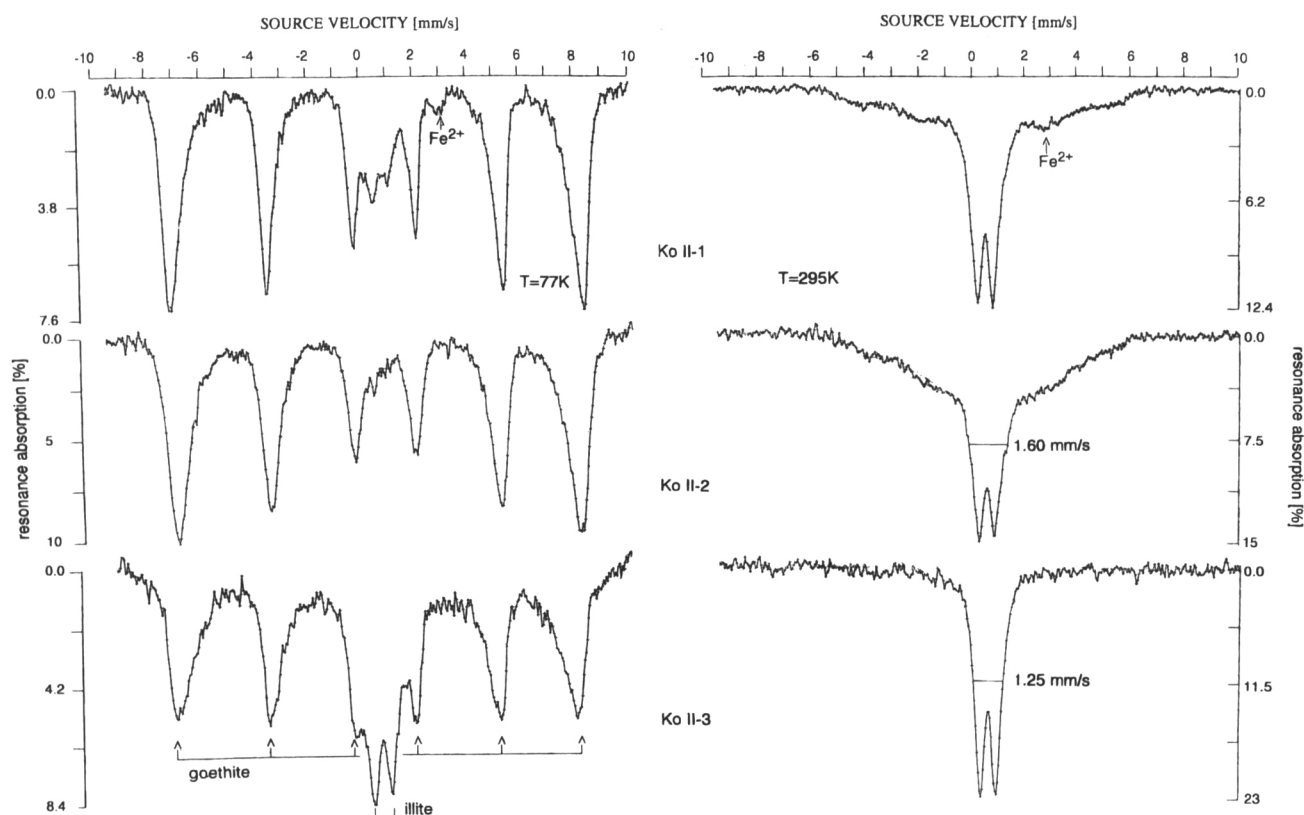
Fig. 2. Mössbauer spectra of samples Ko II-1 (core), Ko II-2 and Ko II-3 (both mantle) at 77 and 295 K. A central doublet dominates MS[295K] that has practically disappeared in MS[77K], where six-line spectra attributed to goethite are most pronounced. The positions of the lines that correspond to the hyperfine field, B', are indicated. A central doublet in MS[77K] of Ko II-1 and Ko II–3 can be ascribed to illite, including the very small Fe^{2+} signal . The illite also contributes to the central doublet in MS[295K] but coincides with that of superparamagnetic goethite.

Table 1. Characteristics of the various samples as determined by XRD and Mössbauer spectra. The line width has not been corrected for instrumental resolution of 0.1°. The goethite content in the core of Ko III and La was too low to measure the reflections.

sample code	line width (°2Θ)			mean XRD line width (°2Θ)	T_N (K)	MS goethite) (weight %)	B' (77 K)
	(020)	(110)	(111)	(130),(021),(121),(140)[1]			
Ko II-1	[2]	0.6 [3]	0.45	0.46	320	20	47.8
Ko II-2	0.35	0.46	0.45	0.57	315	65	47.2
Ko II-3	0.41	0.60	0.60	0.87	300	33	47.1
Ko III-1	not determined			not determined	not measured	2.2	48.5
Ko III-2	0.39	0.31	0.42	0.40	350	70	48.5
Ko III-4	0.47	0.67	0.61	0.74	330	62	47.9
La-1	not determined			not determined	>360	5.0	49.0
La-3	0.26	0.35	0.34	0.35	355	n.m.	48.9
La-4	0.5	0.8 [3]	0.9 [3]	0.95	300	55	48.5
Le II-1	0.20	0.3 [3]	0.5 [3]	0.35	330	17	48.7
Le II-2	0.39	0.59	0.47	0.70	320	66	48.0
Le II-4	0.45	0.90	0.71	0.81	300	56	47.7

[1] these reflections have no interference with quartz.

[2] the second-order reflection of illite may contribute to (020) because of its high concentration in Ko II-1.

[3] the interference of the strong quartz reflections limited an accurate determination of the line width.

Table 2. Munsell hue and other characteristics of the various samples as obtained by INAA (total iron content), measured in Mössbauer spectra (Fe^{2+} fraction and iron compounds), and minerals identified by XRD. The diffraction lines of illite, vermiculite, goethite, hematite, lepidocrocite, siderite, dolomite and feldspar were measured and their relative intensities indicated.

Sample code	Munsell hue	total Fe (wght%)	Fe^{2+} (rel. %)	Fe comp.[1]	XRD analysis[2]						
					i	v	g	l	h	d	f
Ko II-1	2.5YR 6/4	15	5	g, **i**	3+	−	+	−	−	−	−
Ko II-2	7.5YR 3/2	43	0	**g**	+	−	3+	−	−	−	−
Ko II-3	5YR 4/4	27	0	**g**, i	2+	−	2+	−	−	−	−
Ko III-1	2.5Y 7/4	3.4	14	g, **i**	3+	"	−	−	−	−	+
Ko III-2	10YR 3/2	44	0	**g**	+	−	3+	−	−	−	−
Ko III-4	10YR 6/8	39	0	**g**	+	−	+	−	−	−	−
Loam Ko	10YR 6/6	3.1	3	**g**, i	2+	"	−	−	−	−	−
Wa-1	2.5Y 7/4	3.5	36	**g**, i, v	2+	+	−	−	−	−	+
Wa-2	7.5YR 4/4	46	0	**g**, l, i	−	−	3+	3+	−	−	−
Wa-3	10YR 6/3	2.1	10	**g**, i	"	−	−	−	−	−	"
La-1	2.5Y 6/8	5.5	9	**g**, i				n.d.			
La-2	5YR 4/8	n.d.2	0	**g**, l	"	−	4+	2+	−	−	−
La-4	7.5YR 4/4	45	0	**g**	2+	−	2+	−	−	−	"
Le II-1	10YR 6/6	14	10	**g**, l, **i**, v	3+	2+	+	+	−	−	−
Le II-2	10YR 5/8	42	0	**g**	+	−	3+	−	−	−	−
Le II-4	10YR 5/6	35	0	**g**	+	−	3+	−	−	−	+
								s			
Re-1a	2.5YR 3/4	52	0	**g**, h	−	−	4+	−	+	+	−
Re-1	2.5YR 3/9	n.d	0	**g**, h	−	−	4+	−	+	+	−
Re-2	10YR 6/3	n.d.	40	**g**, s	2+	+	+	3+	−	2+	−
Re-3	5YR 5/8	n.d.	2	**g**, i, v	2+	+	2+	−	−	2+	+
Re-4	5YR 5/4	n.d.	4	**g**, i, v	3+	2+	+	−	−	3+	2+

[1] Bold letters (**g** or **i**) mean: dominant in MS.

[2] The intensity is referred to as: very much 4+; much 3+; moderate 2+; present +; questionable "; not proven −. Minerals analyzed: d = dolomite, f = feldspar, g = goethite, h = hematite, i = illite, l = lepidocrocite, v = vermiculite. n.d.= not determined.

tensities of the doublets in MS[77K]. It indicates that the degree of substitution of Fe by Al in illite is higher in Ko II-3 than in Ko II-1 probably because the Fe/Al ratio in the former is higher by a factor of 3 (Table 3).

MS between 77 K and 295 K were measured also during the slow warming up of the cryostat. In each spectrum, the hyperfine field of highest probability, B', was determined by the positions of the steep outer edge of the six individual hyperfine lines, as indicated in MS[77K] of Ko II-3 (Fig. 2). These hyperfine fields are plotted versus temperature in Figure 3. The B' values for Ko II-1 are systematically higher than those for Ko II-2 and the latter are higher than those for Ko II-3. In Figure 3, smooth B'-vs-T curves are drawn through the data points of each sample, and they are extrapolated to zero field beyond 295 K. The shape of these curves is qualitatively similar to that of B in pure goethite (Cornwall, UK). A similarly shaped curve, shown in Figure 3, is the temperature dependence of the hyperfine field in synthetic pure

nanocrystals of goethite with a mean needle width of 9 nm, measured by Van der Kraan (1972). In summary, the crystallite size of goethite in the Ko II samples is systematically smaller from the core outwards.

The total hyperfine fraction (h.f.f.) was determined by the area of the magnetically ordered portion of the spectra relative to the total spectrum. This fraction in each sample is also plotted versus temperature in Figure 3. Both B' and h.f.f. should show extrapolation to zero at the same temperature, which is reasonably fulfilled by the data for Ko II. The extrapolated temperature of the onset of magnetic ordering in goethite in the samples is in the 300-320 K range, which is considerably below the Néel temperature of 393 K for pure goethite and also lower than that of the synthetic nanocrystals, indicating an extremely small crystal size of goethite in Ko II. With decreasing temperature, h.f.f. increases in each spectrum to a maximum at a temperature where magnetic ordering in goethite is complete. The ordered fraction is less than 100% because illite contributes to the non-magnetic part in
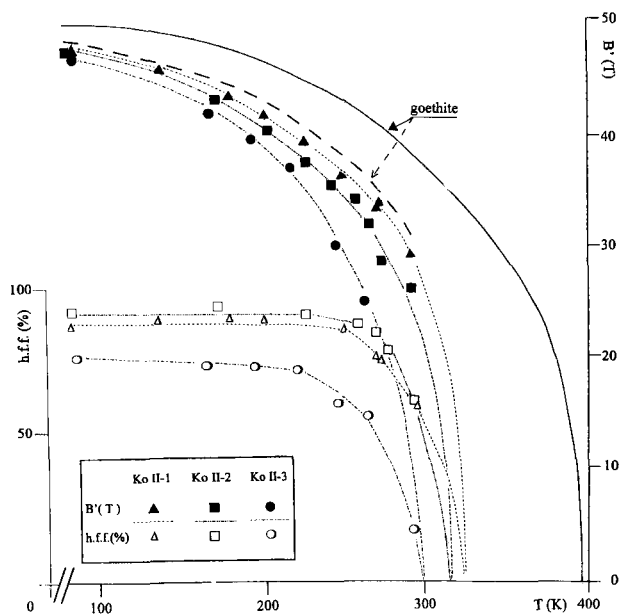
Fig. 3. The magnetic hyperfine field, B', and the hyperfine fraction, h.f.f., in the Mössbauer spectra of Ko II-1, Ko II-2 and Ko II–3 as a function of temperature. The full curve refers to the hyperfine field in a goethite crystal; the dashed curve refers to B' in synthetic goethite nanocrystals with a mean width of 9 nm. Dot-dash lines through the experimental data points of the Ko samples are drawn as a guide to the eye.
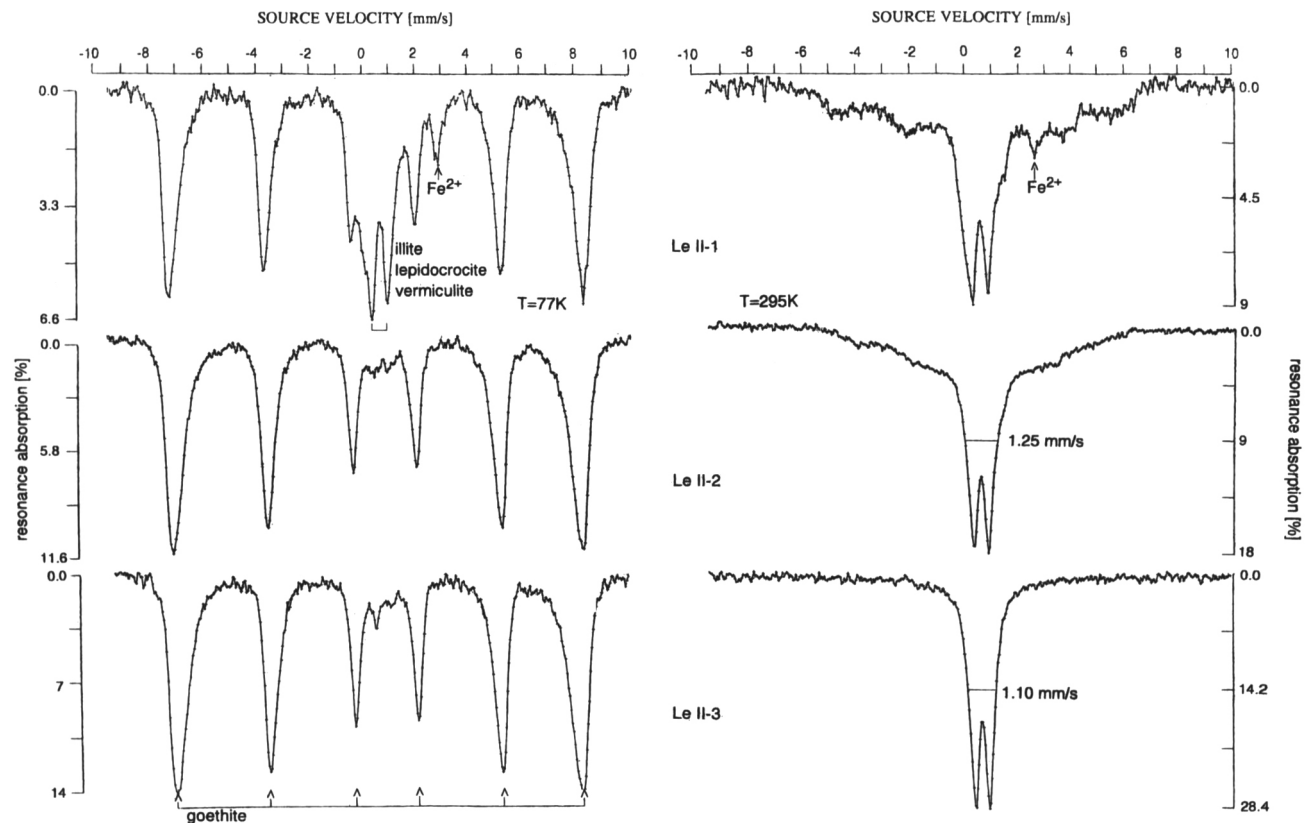
MS. Figure 3 shows that Ko II-3 not only has the lowest temperature of onset of magnetic ordering in goethite, but is also the least homogeneous with respect to goethite-crystallite size distribution, as the temperature range in which magnetically ordered and superparamagnetic phases of goethite coexist is widest. This corroborates the strongly broadened hyperfine lines in MS[77K] of Ko II-3.

MS[295K] and MS[77K] of samples Le II are shown in Figure 4. The spectra have much in common with those of Ko II, particularly with respect to the magnetic properties of goethite. The hyperfine field B'[77K] is highest in Le II-1 and lowest in Le II-3 (Table 1). The non-magnetic part in MS[77K] of Le II-1 is different, however, as it consists of three subspectra, a single Fe^{2+} doublet and two Fe^{3+} doublets. One of the latter can be attributed to lepidocrocite that orders magnetically just below 77 K. This is verified by a measurement of MS at a temperature of 4.2 K. Instead of a single sextet of goethite, a second one was found with a hyperfine field characteristic for lepidocrocite at 4.2 K; XRD confirmed this, and illite and vermiculite were identified in addition (Table 2), contributing to the other two doublets

Fig. 4. Mössbauer spectra of samples Le II-1(core), Le II-2 and Le II–3 (both mantle) at 77 and 295 K. A central doublet dominates MS[295K] that has practically disappeared in MS[77K], where six-line spectra attributed to goethite are most pronounced. The positions of the lines that correspond to the hyperfine field, B', are indicated. The central contribution to MS[77K] of Le II-1 can be assigned to lepidocrocite, illite and vermiculite. The FWHM of the central doublet in MS[295K] is given; note the increase of its line width in the presence of some hyperfine splitting.

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Table 3. Major oxides and a number of trace elements in samples from various rattlestones and loam from Koningsbosch, as obtained by INAA.

sample code	SiO$_2$ (w%)	TiO$_2$ (w%)	Al$_2$O$_3$ (w%)	Fe$_2$O$_3$ (w%)	MnO (w%)	MgO (w%)	CaO (w%)	Na$_2$O w%	K$_2$O (w%)	Ba (ppm)	Cr (ppm)	Th (ppm)	U (ppm)	V (ppm)
Ko II-1	44	0.92	20	21	1.23	1.2	0.22	0.36	3.8	660	n.d.	n.d.	n.d.	n.d.
Ko II-2	22	<0.4	4.6	61	6.9	?	<1.5	0.14	<3.0	4000	310	4	3.9	<150
Ko II-3	31	0.56	13	39	>2.2	1.1	0.14	0.27	2.4	1000	n.d.	n.d.	n.d.	n.d.
Ko III-1	47	1.0	22	4.8	0.10	1.1	0.2	0.4	5.4	590	185	14.1	3.6	175
Ko III-2	10	<0.6	2.7	63	5.5	<2.1	<1.0	<0.1	<8.5	2000	160	2.8	2.6	100
Ko III-3	20	<0.6	1.9	62.5	5.0	<1.8	<0.9	0.1	<7.0	4000	365	2.5	3.7	150
Ko III-4	25	0.3	8.0	56.5	0.4	<0.3	0.3	0.1	1.8	<230	690	5.7	2.8	270
Ko IV-1	51	0.8	17.5	6.2	0.06	0.7	<0.9	0.02	3.6	425	200	12	2.8	150
loam Ko	59	0.8	11.5	4.4	0.07	0.3	0.2	0.3	2.3	250	100	12	2.5	100
Wa-1	67	1.1	19.4	5.6	0.05	2.1	0.12	0.6	3.7	510	145	17	3.9	145
Wa-2	20	<0.8	3.7	65.6	1.7	1.6	<1.2	0.08	<5.5	<350	115	2.8	?	205
Wa-3	86	0.15	4.4	3.1	0.23	0.24	0.05	0.44	1.4	210	n.d.	n.d.	n.d.	n.d.
La-1	68	1.0	17.4	7.7	0.04	1.6	0.26	0.4	3.3	450	n.d.	n.d.	n.d.	n.d.
La-4	?	<0.2	4.6	65	1.55	?	<0.8	0.08	<1.9	655	78	3.5	3.3	95
Le I-1	63	0.8	15.6	15	0.25	0.7	<0.6	0.3	3.6	350	120	12	2.6	125
Le I-3	20	<0.2	3.2	70	2.8	<1.2	<0.9	0.03	<1.8	950	51	2.2	2.5	<60
Le II-1	57	0.7	15.7	20	0.15	1.8	<0.6	0.8	3.4	490	120	12	3	115
Le II-2	25	<0.3	4.8	59.5	1.2	<2.0	<0.8	0.2	<2.5	130	40	4.4	4.7	40
Le II-3	25	<0.7	4.8	57	1.8	1.0	<1.2	0.2	<5.9	225	42	5.8	5.8	40
Le II-4	30	0.3	6.7	50	1.3	<0.8	<0.9	0.25	<4.2	265	51	6.8	5.1	80
S I-1	55	0.9	12.4	11	0.35	<0.3	<0.7	0.3	3.6	435	100	12	4.2	95
S II-1	51	0.8	15.7	26	1.7	1.0	1.0	0.3	2.9	340	n.d.	n.d.	n.d.	n.d
De I-1	80	0,6	6.6	2.4	0.04	<0.6	0.6	1.1	2.9	305	100	7.3	1.7	31
De I-2	35	0.2	2.5	54	0.5	<0.4	0.5	0.4	1.3	200	84	2.5	6.8	200
De I-4	45	0.25	4.2	39	0.12	<0.7	0.5	0.45	<1.7	260	125	3.6	2.4	220
De II-1	67	0.75	15	4.6	0.04	1.0	0.5	1.0	3.8	410	98	12	2.5	100

in MS[77K]. Temperature dependencies of both B' and h.f.f. in samples Le II (Fig. 5) show the same trend as found in Ko II. MS data on Le II suggest that the crystallite size of goethite is largest in the core and smallest in the exterior part of the mantle.

The results of Ko II and Le II are representative for the other rattlestones. Goethite is the predominant iron oxide in all of them, in both core and mantle. The goethite-crystallite size is in the nanometer range, which follows from its superparamagnetic behaviour at 295 K and the dramatic lowering of the magnetic ordering temperature, and is also consistent with what is known from a comparison among common soil minerals (Schwertmann, 1988a). In general, the goethite-crystallite size is smallest and tends to be most heterogeneous in the exterior part of the mantle.

MS were obtained from samples of both surface and core of one of the central segments, Re-1 and Re-1a, and from consecutive shells of the siderite concretions Re-2 through 4. Goethite is the dominant iron oxide in all samples. Siderite was identified in Re-2 only and hematite was present in Re-1 and Re-1a. The goethite crystallinity becomes worse in the shells outwards, in the same way as in the mantle of rattlestones. Hematite in association with goethite has been found in several siderite concretions (Meyer, 1979; Senkayi et al., 1986; unpublished results from the author); hematite has, however, not been identified in any of the rattlestone samples.

X-ray data

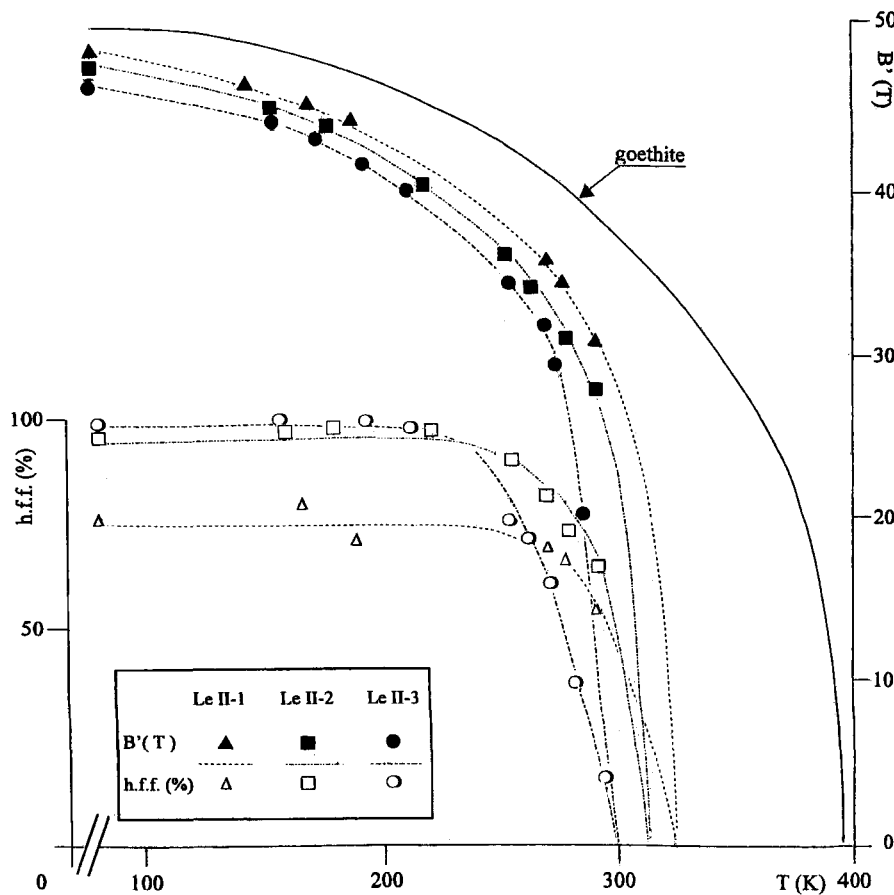In order to verify the Mössbauer results, X-ray diffractograms were obtained from several samples.

Fig. 5. The magnetic hyperfine field, B', and the hyperfine fraction, h.f.f., in the Mössbauer spectra of Le II-1, Le II-2 and Le II-3 as a function of temperature. The full curve refers to the hyperfine field in a goethite crystal. Dot-dash lines through the experimental data points of the Le II samples are drawn as a guide to the eye.

Table 1 lists peak positions and line widths of goethite reflections, and Table 2 lists the mineralogy. The peak positions are similar to those of pure goethite, which makes isomorphic substitution of Fe by Al unlikely. The (020), (110) and (111) lines and the average of the (130), (021), (121) and (140) lines of goethite were chosen to investigate line broadening. Although the first three lines in the core samples were subject to interference with strong quartz lines, the other four lines are not. A systematic increase in line broadening is observed in the samples Ko II and Le II from the core outwards, as shown in Table 1, indicating a decrease in crystallinity (Schwertmann, 1988a), consistent with MS data. XRD data on line broadening in goethite in the mantles of Ko III and La show a similar trend. The goethite content in the core of these rattlestones was too low to determine the former. The weight percentage of goethite in each sample was derived from the absolute Fe content, determined by INAA, in combination with the goethite fraction measured in MS[77K]. In addition, the temperature of onset of magnetic ordering in goethite, T_N, is presented in Table 1. The lower this temperature, the poorer the goethite crystallinity (Murad & Bowen, 1987) consistent with the stronger line broadening found.

In both MS and XRD, lepidocrocite was identified in several samples from rattlestones found at sites north of the Meuse river (Table 2). Lepidocrocite was mostly encountered in the mantle, except in Le II-1. The line width of the (020) reflection is reasonably narrow and hence lepidocrocite is more crystalline than goethite in these samples. Moreover, this iron oxide is rarely evenly distributed over the whole soil matrix (Schwertmann, 1988b). This might explain why lepidocrocite was found in some laminae but is absent in adjacent ones. Lepidocrocite is not found in rattlestones from sites east of the Meuse, although Riezebos et al. (1978) suggested that this iron oxide is a constituent in middle terraces in south Limburg.

XRD results on clay mineral identification are given in Table 2, where they are also compared with MS results. The overall correspondence is good. Besides goethite, illite is found in most samples, not surprisingly, as it is the main clay mineral in Dutch soils (Edelman & De Bruin, 1986). Vermiculite, identified by XRD in some core samples, can be associated with a relatively high Fe^{2+} signal in MS. Table 2 also lists the XRD results on the siderite concretion. With respect to the iron compounds they are consistent with MS. All Re samples contain dolomite, which is absent in the rattlestone samples. Clay minerals were encountered only in the shells of the concretion.
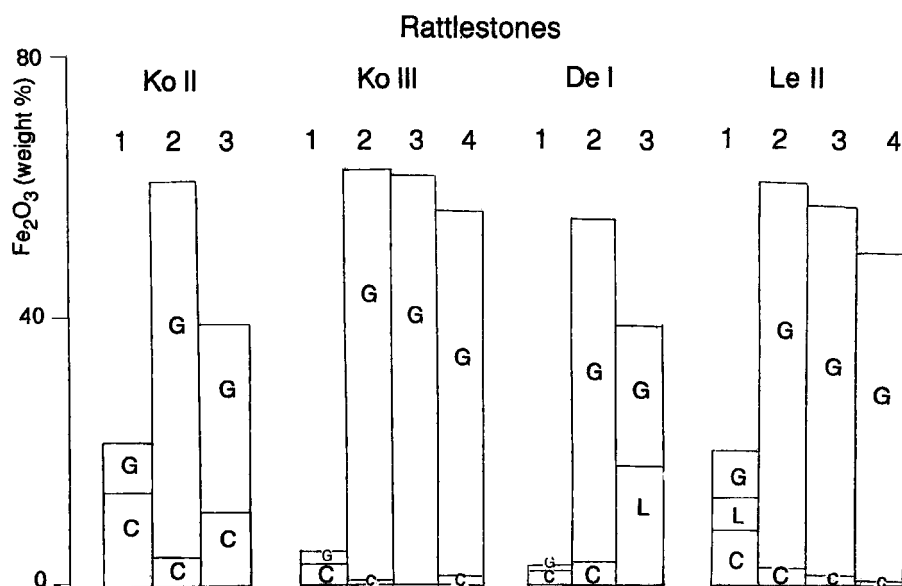
Fig. 6. Histogram showing the content of the iron compounds in four rattlestones in terms of weight percentage of Fe_2O_3. The absolute Fe content was obtained by INAA; the relative amount of iron compounds was determined from MS[77K]. Code 1 refers to the core and codes 2-4 to different laminae in the mantle of each rattlestone. The mantle is 5-10 mm thick.
G = goethite, L = lepidocrocite and clay minerals, mainly illite.

INAA data

Elemental composition of the samples has been obtained by INAA. The Fe content in the core varies from 18% by weight in S II to 1.7% in De I; the latter has hardly any Fe accumulation at all. In contrast, the Fe content in the core segment of the siderite concretion is 52% by weight. The mantle of rattlestones has a high iron accumulation (up to 50% by weight) that varies by less than a factor of 2 among the various samples (except for Wa-3). The Fe content relates to that of Al as shown in Figure 6; in general, a high content in the former corresponds to a low content in the latter and vice versa. The amount of Fe gradually decreases in each rattlestone in consecutive layers of the mantle outwards, while the content of various other elements just increases. A histogram (Fig. 7) illustrates how the total Fe content in core and mantle of four different rattlestones is distributed among goethite, lepidocrocite and clay minerals, as determined in MS. Goethite is the predominant iron oxide; lepidocrocite has been identified only in the rattlestones from north of the Meuse river (De I and Le II). The composition in terms of major oxides (in weight percentage) and a few trace elements (in ppm) is presented in Table 3.

The amount of silicon in the core is about twice that in the mantle, which is understandable as the much higher Fe accumulation in the mantle lowers the relative Si content in the latter. A quantitative estimate of illite has been made, assuming that K is fully associated with this clay mineral by using the chemical formula, $KAl_3Si_3O_{14}H_4$. The illite content in the core in general exceeds that in the mantle by a substantial factor, and it tends to increase gradually outwards in the latter. This could be a reason why several

trace elements show a similar trend: the amount of Rb and Cs, for instance, is positively correlated with illite, which is consistent with previously reported results (Moura & Kroonenberg, 1990).

Heavy metals can, as a rule, be associated with Fe hydroxides – supplied by groundwater – that remain
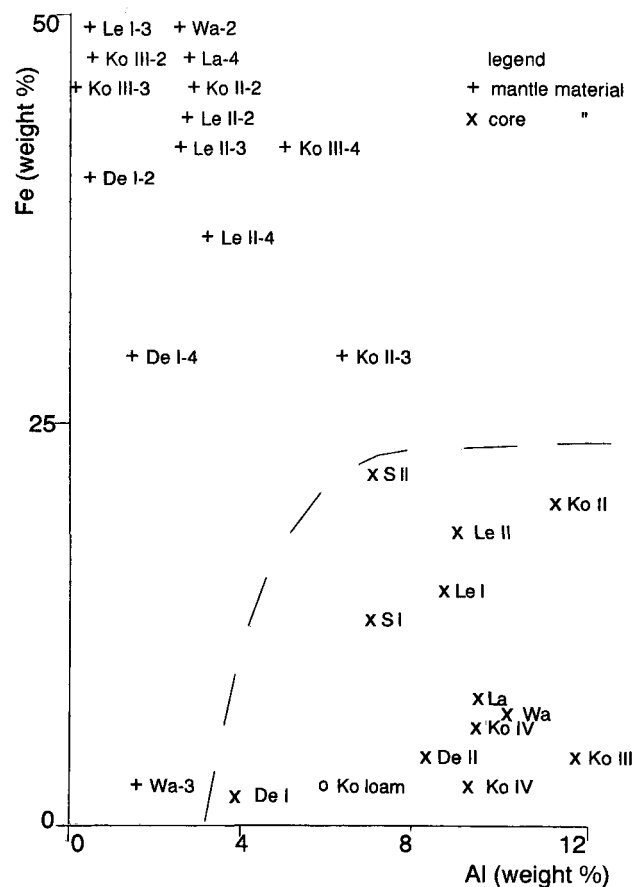

Fig. 7. A plot of the total Fe versus Al content, obtained by INAA, in core and mantle of the rattlestones (indicated by their codes). Below the dotted line are the Fe and Al content of the core samples. Clayey loam from the Koningsbosch site is indicated by (o).

incorporated in the iron oxide after sedimentation. The element Ba is also positively correlated with illite and the ratio Ba(ppm)/K_2O is similar to the value for subsurface sediments in the southern Netherlands (Huisman et al., 1997). In the samples Ko II-2, Ko II-3, Ko III-2 and Ko III-3, however, Ba is very strongly accumulated (Table 3). Such irregular accumulations of Ba without correlation with illite or Fe may indicate that it is present as a separate mineral phase or that it is built into the Fe-oxide structure in varying ratios to iron (Huisman, 1998). Samples with an excessively high Ba content show a high Mn content, too. It follows also from Table 3 that the distribution of Th and U in core and mantle is different; the mean ratio Th/U amounts to 4 in the core and is about 1 in the mantle. These elements tend to fractionate because of oxidation of U to soluble ions, and because of selective adsorption of Th in clays and its retention in heavy resistant minerals (Wedepohl, 1978).

The mean content of the rare earth elements in the mantle is systematically higher than in the core, except for La, Ce and Nd, which elements show an opposite behaviour. The shale-normalised REE patterns for both core and mantle are shown in Figure 8 and compared with that reported for shallow groundwater

in the Netherlands (Huisman et al., 1999). It appears that the pattern in the mantle is similar to that in groundwater. The relative depletion of LREE in the mantle is attributed to the fact that they form less easily carbonate complexes than HREE, due to their larger ionic radii. It is known that bicarbonate ion pairs can play an important role for the solution chemistry of HREE, which explains a significant relative fractionation and an enrichment in the latter (Michard et al., 1987). The pattern in the core, on the other hand, is more shale-like without significant fractionation, which is more common for river water (McLennan, 1989). In summary, the mantle has been formed from elements that are mainly supplied by groundwater, whereas those in the core originate primarily from the river water. In this connection it is noted that loam from Koningsbosch also has a shale-like REE pattern.

Variations in the content of heavy metals within the mantle and between various rattlestones are probably caused by differences in groundwater composition during the formation of these stones. Such diverseness could be the result of differences in aquifer material, and by changes in pH and Eh of the groundwater.

Munsell hues of iron oxides

The Munsell hue of the samples, using the Munsell soil color charts (1954) is also indicated in Table 2. The color of the iron oxide may vary from sample to sample and often has sufficient consistency to be useful for the identification of these oxides in soils and sediments (Schwertmann, 1988a). The mineral-specific Munsell hues of iron oxides in soils are in the following ranges: hematite 5R-2.5YR, lepidocrocite 5 YR-7.5YR, and goethite 7.5YR-2.5Y, sometimes extending to 5YR.

Finely dispersed soil goethite and lepidocrocite usually become increasingly dark with poorer crystallinity; goethite crystals smaller than 50 nm, for instance, are brownish (Cornell & Schwertmann, 1996). The first number behind the color hue, called the value, is a notation for darkness varying between 0 (absolute black) and 8 (absolute white). Core samples have a higher value than those of the mantle, which is qualitatively consistent with the better crystallinity of goethite in the former.
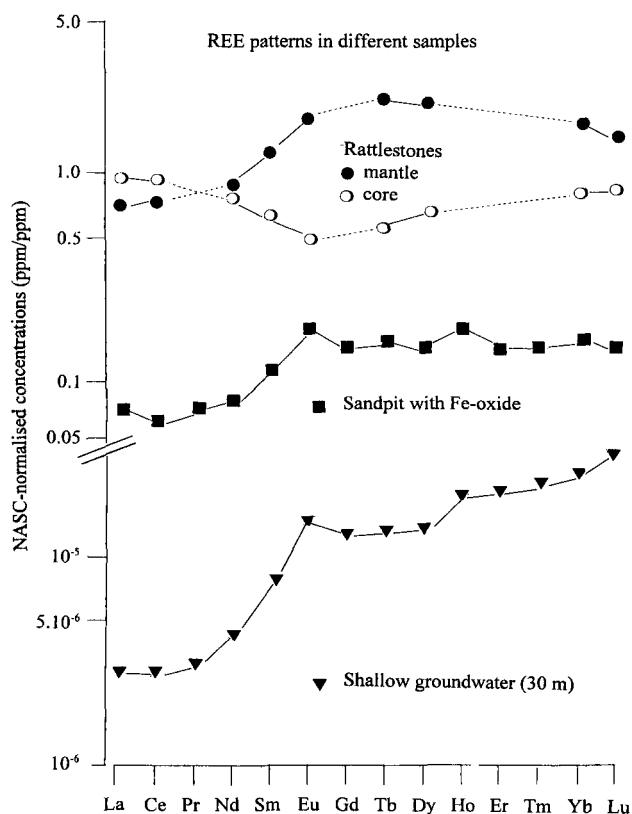

Fig. 8. REE patterns in core and mantle of rattlestones obtained by INAA are compared with the patterns found in shallow groundwater and in a sandpit. The concentrations are normalised using NASC data.

Discussion

Goethite forms in all soil types and in early stages of weathering it is the most commonly found iron oxide. Dissolved ferrous iron, which is usually present in re-

duced sediments, oxidizes to Fe(III) when it encounters oxygen and converts to virtually insoluble Fe(III) oxyhydrates (Cornell & Schwertmann, 1996). In alternating reducing and oxidizing conditions, a clay layer in a sandy matrix will accumulate these hydrates through the following process. When the sediment layer is reduced, Fe(II) is distributed evenly in the aqueous phase. When this sediment dries out, iron will partially precipitate, being exposed to oxygen, while the concentration in the remaining solution increases. Eventually the finer layers will still contain water and its dissolved iron. Upon complete dryout, this iron precipitates at the contact of the fine layer (which is still water-saturated) and its aerated coarse surroundings. This is a repetitive process. In addition to accumulate iron, the clay layer may fracture upon drying out, whereby each of the fragments will become a nucleus of Fe accumulation. With time, the accumulated iron may form a rigid oxide coating around the clay core, and become a concretion. When the concretion dries out further, the clay core will shrink and detach from the mantle, thus forming a cavity in the stone. Because the inner part of the rattlestone is not subject to periodical reduction and precipitation any more, it can recrystallize to larger size, while this is not the case for the active outer part (Van Breemen & Buurman, 1998). These processes are governed throughout the year by groundwater so that absolute accumulation of iron, conveyed from surrounding areas, may occur. As a result of fluctuating groundwater levels, yellowish brown goethite concentrates form laminae in the mantle of the stone with an Fe(III)-oxide content that is high relative to the surroundings. These oxides may cement the mineral grains giving rise to the hardness of the concretion.

The size of the cavity will depend on the amount and mineralogy of the clay, and the original water content. Since illite is the dominant clay mineral, its content in the core is positively correlated with the size of the cavity in the rattlestones as can be seen by comparing Figures 1 and 6.

The former process of genesis of rattlestones is entirely different from the suggestion by Van der Burg (1969) that they have been formed as a result of the oxidation of siderite concretions that had been deposited contemporaneously with the sediments in the beds where they are found today. As siderite is particularly vulnerable to weathering under atmospheric conditions, it will oxidize preferentially to goethite (Pettijohn, 1975). Although MS and XRD results with respect to goethite crystallinity in the siderite concretion are qualitatively similar to those obtained with rattlestones, both systems differ in several aspects: (1) the iron content in the central segments of the concretion is very high and clay minerals are absent in contrast to what is found in the core of rattlestones, (2) hematite is found in the central segments and absent in the rattlestone samples, (3) the latter may contain a strong and sometimes irregular accumulation of heavy metals such as Ba, which is unlikely in siderite as its structure cannot accommodate any accumulation of heavy metals (Huisman, 1998), and (4) the specific density of rattlestones can, due to a large cavity, be much smaller than the densities reported by Van der Burg (1969), as shown in Figure 1. Septarian cracks have indeed been found in the alterated siderite concretion, which result in a relatively small cavity only. These differences make it unlikely that rattlestones are the result of oxidation of siderite. It examplifies what Fitzpatrick (1988) has described as iron compounds being indicators of pedogenic processes.

Rattlestones are composed of clay minerals, mainly illite and vermiculite, and poorly crystalline goethite. The main non-clay mineral is quartz. This mixture closely corresponds with what was called an assemblage of young, moderately weathered soils in temperate regions by Van Breemen & Buurman (1998). The official definition of a rattlestone given in the introduction (Jackson, 1997) will be more in accordance with the actual results when it is recognized that the core material does not consist of loose sand only.

The elemental analysis of several samples of a rattlestone gives additional geochemical information on the subsurface soil and sediments of the sampling area. For example, the higher accumulation of various heavy metals in rattlestones from the older floodplains east of the Meuse river compared to that in stones from north of the river indicates a richer mineralogy in the former. On the other hand, the absence of lepidocrocite in rattlestones from Koningsbosch might imply that this iron oxide has been transformed into goethite in the course of time though this process is very slow under pedogenic conditions (Schwertmann & Taylor, 1972). As lepidocrocite occurs predominantly in younger postglacial soils following Schwertmann & Taylor (1971), the reason for its absence is because these rattlestones are from the much earlier Sterksel Formation (Middle Pleistocene). Lepidocrocite was not found in the siderite concretion.

Conclusions

The chemical and mineralogical composition of rattlestones found near the main Dutch rivers has been extensively studied by Mössbauer spectroscopy, INAA and XRD. Rattlestones are iron concretions

formed in an environment of lateral accumulation of Fe under the influence of periodical oxidation, around a fine core of ferruginous sediments, mainly clay and sand. The core has shrunk and detached itself from the mantle around it. The cavity formed can have a considerable size, of up to 50% by volume. ^{57}Fe Mössbauer spectroscopy was applied to identify the iron oxides, among which goethite is predominant. The goethite crystallinity was investigated by making use of its magnetic properties and showed to be poorest in material from the outer edge of the rattlestone. The latter is confirmed by broadening of the various X-ray reflections. In addition, illite and vermiculite were identified by XRD; they were found mainly in the core.

The elemental composition was determined by INAA. The iron content in the mantle is about 50% by weight and gradually decreases outwards, while the core contains 2-15% Fe by weight. Differences between rattlestones from a Middle Pleistocene site east of the Meuse river and those from Late Pleistocene sites north of the river are the absence of lepidocrocite and a richer mineralogy in the former. As a result of fluctuating groundwater levels, iron and other (trace) elements were supplied and could lead to concentrates, of iron hydroxides in particular, in the most porous parts of the clayey sediment. The detailed mechanism describing the formation of rattlestones is consistent with experimental results. Its genesis is from inside outwards and is difficult to reconcile with the concept of oxidation of a siderite concretion.

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