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Investigation of bog iron ores from Sømarken, Denmark

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Abstract

Seventeen samples of bog iron ores were submitted for investigation. The magnetic susceptibility of all the samples was measured and four of the samples were also investigated by X-Ray diffraction.

The XRD data demonstrated considerable mineralogical variation between the samples, but all were dominated by poorly crystalline goethite. The background variation made comparison of the iron oxide mineralogy very difficult, and the complexity of the signal meant that obtaining good estimation of peak heights for the various iron minerals was not possible with any degree of confidence. All four examined samples contained some magnetite, one (X16a) in significant quantity. X16a also contained traces of hematite.

In contrast, the magnetic susceptibility data showed a clear distinction between samples with very low levels of paramagnetic minerals (magnetite, maghemite)with mass specific magnetic susceptibility of <50 SI (10^{-8}) and those with values of >8000 SI. A few samples had intermediate values. The samples with high values of susceptibility had values in the same range as those previously reported for roasted siderite iron ores.

Samples with low magnetic susceptibility are X12, X15, X17, X19, X22 and x31. Samples with intermediate susceptibility are x9, X10, X13, X16b, X25, x36. Samples with high magnetic susceptibility are x9b, X16a, X18, X26, and x37.

Contents

Methods

Samples were crushed and then the powders investigated by two separate techniques.

Four of the samples (X10, X13, X16a, X16b) were investigated by X-Ray diffraction using Philips Automated Powder Diffractometers on bulk powder specimens. The diffractograms were collected digitally, with averaged readings at 0.1606° intervals, and are presented graphically in Figure 1. Initially diffractograms were collected using a copper tube (Cu Kα, $\lambda = 1.542$ Å), but the data contained noise spikes due a faulty tube. Replacement data were collected on a different diffractometer, equipped with a cobalt tube (Co Kα, $\lambda = 1.790$ Å), but which lacked a monochromator. The data from the cobalt tube are illustrated here (Figure 1). Interpretation of the diffractograms was undertaken manually, employing data from the online AMCSD database (Downs & Hall-Wallace 2003), with further data on iron oxides from Cornell & Schwertmann 2003.

The magnetic susceptibility of all the powders was measured with Bartington MS2 magnetic susceptibility meter using a dual frequency MS2b sensor. Samples were weighed and the raw results converted to a mass specific susceptibility in SI units. Low frequency measurements were made at 0.46kHz and high frequency measurements at 4.6kHz.

Both techniques were undertaken using equipment of the School of Earth and Ocean Sciences, Cardiff University, Wales, UK.

Results

X-Ray diffraction

The diffractograms for the analysed specimens are presented in Figure 1, with the principle peaks listed in Table 1.

Sufficient peaks are present to indicate that the main iron-bearing mineral is goethite (Table 3). One consequence of heating bog iron ores would be the dehydration of goethite to hematite. Overlap in peak position means that it has not been possible to identify hematite with certainty in most samples. The 2.592 Å hematite peak does seem to be present in X16a, as does the 3.684 Å peak.

Identification of the paramagnetic minerals is more problematic (Table 4). Major magnetite peaks ought to be present at 2.97 Å (the 220 peak, relative intensity 30), 2.53 Å (the 311 peak, relative intensity 100), 1.62 Å (the 511 peak, relative intensity 30) 1.71 Å (the 422 peak, relative intensity 10) and 1.48 Å (the 440 peak, relative intensity 40). Maghemite should show major peaks at 2.95 Å (the 220 peak, relative intensity 30), 2.51 Å (the 313 peak, relative intensity 100), 2.09 Å (the 400 peak, relative intensity 15), 1.60 Å (the 513 peak, relative intensity 20) and at 1.47 Å (the 440 peak, relative intensity 40). The situation is further complicated because it is likely that any magnetite would show some degree of aluminium substitution (solid solution with hercynite) which would reduce the spacings slightly. The peaks for two minerals are very similar (Table 3), and given the relatively low peak heights distinction using the absence of a 2.09 Å peak to suggest magnetite is present, rather than maghemite, must remain rather tentative approach.

The paramagnetic minerals (probably magnetite) appear to be present in low quantities in X10 and X13, but are much more prominent in X16a. The main peak is only just distinguishable in X16b, suggesting a very low proportion in this sample.

The non-ferruginous minerals are variable in abundance, with quartz in particular abundance in X10 and X16b. X13 shows several peaks that have not been able to be fully identified, but are probably produced by a feldspar. X13 also contains a moderate amount of quartz. X16a contains only a very small proportion of quartz. Small peaks occur at about 7° 2theta in all the samples, suggesting the presence of a clay mineral with a 14 Å basal spacing; this is likely to be chlorite.

Magnetic susceptibility

Results of the MS measurements are given in Table 4. A wide range of mass specific MS (χ, in SI units, 10^{-8} m^3 kg^{-1}) was recorded, ranging from 35 to 13017 for the low frequency measurements (χ_{lf}) and 30 to 12165 at high frequency (χ_{hf}). The frequency dependence (expressed as $\chi_{fd}\% = (\chi_{lf}-\chi_{hf})*100/\chi_{lf}$) was generally low, but five samples showed a high frequency dependence. Four of these values are suspect as they occur in materials with low susceptibility, and hence are most at risk from instrumental errors. Another potential source of error is if any of the samples contain small quantities of metallic iron. Frequency dependence is indicative of the degree to which superparamagnetic particles of a grain size <0.03µm are present.

Six of the samples show very low magnetic susceptibility, with χ less than 50 (X12, X15, X17, X19, X22, X31). These samples must contain very little magnetite or maghemite. Five samples have extremely high magnetic susceptibility with χ greater than 8000 (X9b, X16a, X18, X26, X37). These samples must contain a very high proportion of paramagnetic minerals, most likely magnetite. A closely comparable value for χ of 3510 to 12810 was recorded for roasted siderite by Vernon (2004).

The remaining samples (X9, X10, X13, X16b, X25, X36) have intermediate magnetic susceptibility. The intermediate samples might indicate samples without such a high proportion of conversion of the iron oxides into magnetite, or might indicate samples with a lower proportion of iron oxides. Indeed both factors are probably at play.

Interpretation

XRD has proved rather problematic in interpreting the samples, but some conclusions can be drawn. Goethite appears to be the major iron-bearing mineral in all the samples. The goethite peaks are broad, suggesting poor crystallinity. Magnetite appears to be present in all the samples in trace amounts, but in a rather larger proportion on X16a. This same sample also shows a small proportion of hematite.

The magnetic susceptibility measurements give a clearer picture of the development of the paramagnetic minerals within particular samples:-

- Five samples have χ greater than 8000 (X9b, X16a, X18, X26, X37). One of these, X16a, was also the sample showing XRD evidence for significant development of magnetite and traces of hematite.

- Six samples (X9, X10, X13, X16b, X25, X36) have intermediate magnetic susceptibility and three of these (X10, X13, X16b) showed varying traces of magnetite in XRD. Unfortunately the nature of the traces meant it was not possible to attempt any correlation between magnetite peak height and χ.

- Six of the samples show χ less than 50 (X12, X15, X17, X19, X22, X31). These samples must contain almost no magnetite or maghemite, but unfortunately none of these was examined by XRD.

On this basis, it is likely that eleven of the samples have been altered to a greater or lesser extent by heating, whilst six are essentially unaltered.

The iron minerals are superimposed on a variable detrital mineralogy including quartz, chlorite and feldspar.

References

Cornell, R.M. & Schwertmann, U., 2003. *The iron oxides; structure, properties, reactions, occurrences and uses*. 664pp. Wiley.

Downs, R.T. and Hall-Wallace, M., 2003. The American Mineralogist Crystal Structure Database. *American Mineralogist*, **88**, 247-250.

Vernon, R. 2004. *Application of archaeological geophysical techniques to the investigation of British smelting sites*. Unpublished PhD thesis, University of Bradford

	X10		**X13**		**X16a**		**X16b**	
identification	*2theta*	*d*	*2theta*	*d*	*2theta*	*d*	*2theta*	*d*
14.2 chlorite 001 (85)	7.0	14.6	7.0	14.6	7.0	14.6	7.0	14.6
4.26 quartz 100 (20)	24.43	4.23			24.43	4.23	24.59	4.20
4.18 goethite 110 (100)			24.75	4.18				
					25.10	4.12	25.07	4.12
3.68 hematite 012 (30)					28.12	3.68		
3.34 quartz 101/011 (100)	31.34	3.31	31.34	3.31	31.18	3.33	31.34	3.31
3.19 feldspar 002 (100)			32.62	3.19				
3.14 feldspar 220 (45)			33.10	3.14				
2.97 magnetite 220 (30)			35.84	2.91				
			37.92	2.75				
2.69 goethite 130 (47)	38.88	2.69	38.89	2.69	39.05	2.68	39.05	2.68
			39.37	2.66				
2.59 hematite 110 (70)					40.40	2.59		
2.58 goethite 210 (12)					40.81	2.57		
2.53 magnetite 311 (100)	41.62	2.52			41.62	2.52	41.78	2.51
	41.94	2.50	41.94	2.50				
2.49 goethite 400 (10)					42.10	2.49	42.40	2.48
2.45 goethite 111 (78)	43.06	2.44	43.06	2.44	43.22	2.43	43.06	2.44
							43.54	2.41
							46.60	2.26
2.25 goethite 121 (10)			47.24	2.23			47.24	2.23
					47.40	2.23		
							47.56	2.22
					48.20	2.19		
2.19 goethite 140 (18)					48.36	2.19	48.36	2.19
			48.68	2.17				
							49.98	2.12
1.98 quartz 021/201 (3)	54.14	1.97						
1.81 quartz 112 (13)	59.28	1.81					58.32	1.81
							59.44	1.81
1.80 goethite 211 (11)					59.60	1.80	59.76	1.80
							62.33	1.73
1.72 goethite 221 (38)	62.65	1.72			62.65	1.72		
1.71 magnetite 422 (10)			63.14	1.71	63.30	1.71	63.14	1.71
							63.62	1.70
1.69 goethite 402 (6)	63.94	1.69			63.94	1.69	63.94	1.69
	64.10	1.69						
1.67 quartz 022 (3)					64.74	1.67		
1.66 goethite 600 (3)	65.22	1.66			65.06	1.66	65.22	1.66
1.60 goethite 402 (6) /1.61 magnetite 511 (30)			68.44	1.59	68.44	1.59		
1.56 goethite 151/601 (26)			70.20	1.56	70.04	1.56		
							70.52	1.55
1.54 quartz 211/121 (9)	71.33	1.54						
					71.49	1.53	71.49	1.53
1.51 goethite 002 (12)			73.25	1.50	73.42	1.50		
1.48 magnetite 440 (40)					74.86	1.47		
1.45 quartz 113 (2)	75.34	1.46	75.34	1.46	75.34	1.46		
			75.50	1.46			75.99	1.45
1.45 goethite 061 (12)	76.31	1.45	76.31	1.45	76.47	1.45	76.47	1.45
					76.95	1.44		
1.42 goethite 121 (2)	78.39	1.42					78.39	1.42
			79.36	1.40				

Table 1. Summary of diffraction peaks, using Co Kα radiation. Interpretation list the spacing, mineral, index and relative intensity (in brackets) as given by the AMCSD files.

Hematite			*Goethite*		
d (Å)	*hkl*	*I*	*d (Å)*	*hkl*	*I*
3.684	**012**	**30**	4.98	200	12
2.700	104	100	**4.183**	**101**	**100**
2.592	**110**	**70**	3.383	201	10
2.207	113	20	2.693	301	35
1.841	024	40	2.583	210	12
1.694	116	45	2.489	400	10
1.599	018	10	2.450	111	50
1.486	214	30	2.253	211	14
1.454	300	30	2.190	401	18
			1.719	212	20
			1.564	511	10

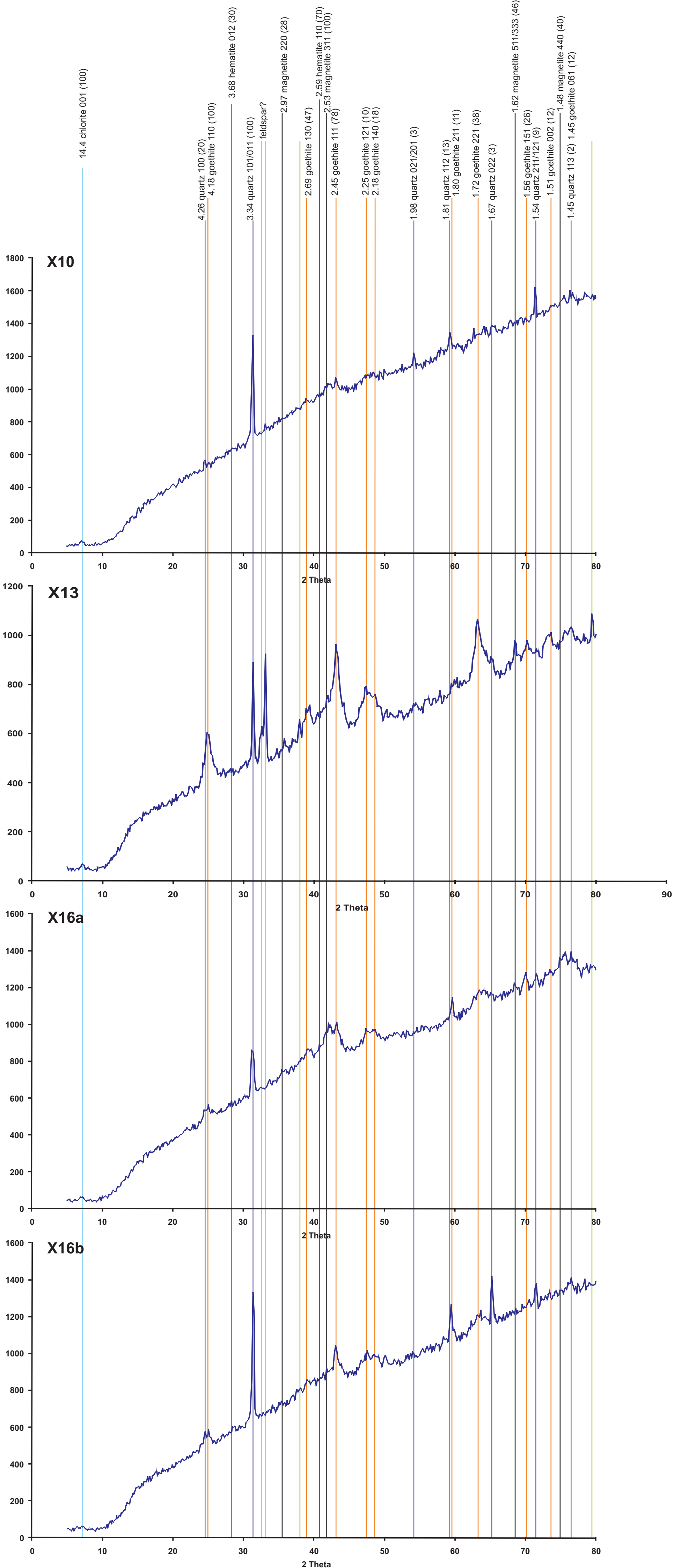
Table 2. Evidence for identification of the diamagnetic iron minerals goethite and hematite (data from Cornell & Schwertmann, 2003).
Peaks are only listed where they have a relative intensity for the mineral of >10.
Grey tone indicates peaks which are not recognisable within the traces.
Peak in bold is a strong identification. Other peaks are ambiguous.

Magnetite			*Maghemite*		
d (Å)	*hkl*	*I*	*d (Å)*	*hkl*	*I*
2.967	220	30	2.95	220	30
2.532	311	100	2.514	313	100
			2.086	400	15
1.715	422	10	1.701	426	9
1.616	511	30	1.604	513	20
1.485	440	40	1.474	440	40

Table 3, Evidence for the identification of the paramagnetic minerals magnetite and maghemite (data from Cornell & Schwertmann, 2003).
Peaks are only listed where they have a relative intensity for the mineral of >10.
Grey tone indicates peaks which are not recognisable within the traces.
Other peaks are ambiguous.

	low	high	weight(g)	χ_{lf}	χ_{hf}	χ_{fd}%
X9	123	98	16.35	75	60	20.3
X9B	7856	7019	6.15	12774	11413	10.7
X10	3707	3554	9.86	3760	3604	4.1
X12	57	48	15.99	36	30	15.8
X13	886	850	3.52	2517	2415	4.1
X15	63	52	17.21	37	30	17.5
X16A	7587	7291	7.17	10582	10169	3.9
X16B	224	205	12.67	177	162	8.5
X17	66	61	18.91	35	32	7.6
X18	6941	6631	8.65	8024	7666	4.5
X19	50	47	13.33	38	35	6.0
X22	78	75	17.84	44	42	3.8
X25	567	534	6.81	833	784	5.8
X26	4478	4185	3.44	13017	12166	6.5
X31	62	61	13.49	46	45	1.6
X36	2285	1870	6.87	3326	2722	18.2
X37	9693	9297	8.18	11850	11366	4.1

Table 4. Magnetic susceptibility measurements at low and high frequency, with conversion to mass-specific susceptibility (χ_{lf} and χ_{hf}).


14.4 chlorite 001 (100)
4.26 quartz 100 (20)
4.18 goethite 110 (100)
3.68 hematite 012 (30)
3.34 quartz 101/011 (100)
feldspar?
2.97 magnetite 220 (28)
2.69 goethite 130 (47)
2.59 hematite 110 (70)
2.53 magnetite 311 (100)
2.45 goethite 111 (78)
2.25 goethite 121 (10)
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1.98 quartz 021/201 (3)
1.81 quartz 112 (13)
1.80 goethite 211 (11)
1.72 goethite 221 (38)
1.67 quartz 022 (3)
1.62 magnetite 511/333 (46)
1.56 goethite 151 (26)
1.54 quartz 211/121 (9)
1.51 goethite 002 (12)
1.48 magnetite 440 (40)
1.45 quartz 113 (2)
1.45 goethite 061 (12)
X10
0
200
400
600
800
1000
1200
1400
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1800
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2 Theta
X13
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2 Theta
X16a
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1600
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2 Theta
X16b
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1200
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80
2 Theta

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