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Chemical and visual analysis of flint from Gotland and Öland

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We have used visual and instrumental (EDXRF, energy-dispersive x-ray fluorescence) methods to analyse naturally occurring flint from Gotland and Öland. We compare the results with previously published analyses conducted on other types of flint. We identify two visually distinct types of flint from Gotland: grey and white/brown flint. The chemistry of the more common grey flint is unique compared with other Scandinavian flint types. The chemistry of the white/brown flint is similar to other types of Scandinavian flint, although its visual appearance is unique. Both flint types from Gotland are distinct from Ordovician flint from Öland, both in regard to visual properties and to chemical composition. At present we are unable to identify the geological origin of flint from Gotland.

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Flint occurs only sparingly on the Baltic islands of Gotland and Öland. It consists of small rolled nodules whose size significantly limits the kinds of stone tools that could have been produced from them. Nevertheless, flint from Gotland and Öland has been reported to have been used for tool making during prehistory (Österholm 1989; Alexandersson et al. 1996). For example, Rundkvist with colleagues (2004, p. 17 ff) reports on Middle Neolithic flake production from multifacial and bipolar cores from the site Rojrhage on southern Gotland.

Flint from these islands has been described previously (Laufeld 1971; Königsson 1973; Tralau 1974; Österholm 1989; Alexandersson et al. 1996; Alexandersson 2001; Högberg & Olausson 2007), but no visual and chemical comparison with other flint types has previously been carried out. This paper presents the results from such an analysis, showing that: 1) samples from Gotland represent two visually different flint types (which we term grey flint from Gotland and white/ brown flint from Gotland); 2) these types are chemically different; 3) the grey flint from Gotland is a chemically unique flint not previously described; 4) flint from Gotland and Öland can be differentiated on the basis of chemistry as well as appearance; 5) there is a modest chemical similarity between samples from Gotland and one sample from Öland; and 6) some chemical overlap exists between the white/brown flint from Gotland and flint from south-western Scandinavia.

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Fig. 1. Schematic cross-section of the geology of the Baltic Sea basin across the islands of Öland and Gotland. Adapted from Eliason 2010, p. 18.

Geology and flint types

The geological formations that make up the islands of Gotland and Öland were formed during the Cambrian, Ordovician and Silurian Periods of the Palaeozoic Era, 444–416 million years ago (Eliason 2010). Fig. 1 gives a general overview of the geological conditions, showing that Gotland's bedrock was formed of Silurian deposits which owe their existence to an ancient coral reef. No reports of flint formations in this bed-rock are known (Eliason 2010). By contrast, the bedrock of Öland was formed during the Ordovician and flint nodules do occur, albeit rarely, in the limestone bedrock here (Högberg & Olausson 2007).

Ordovician flint from Öland has a distinctive appearance. It comes in a variety of colours; white, grey, brown and reddish (Högberg & Olausson 2007, p. 136 ff). Normally it has a homogeneous structure and a smooth flaked surface. Its reflectivity varies from shiny to matte. A special characteristic of the flint is the oily appearance of a freshly flaked surface. In a previous study (Hughes et al. 2012) we have characterised the chemical composition of this flint and documented its distinctiveness from other Scandinavian flint types.

Flint has been encountered on Gotland in the form of rolled nodules on beaches. It has not previously been described in detail and no chemical characterisation has been done. As mentioned above, the bedrock of Gotland consists of Silurian sediments without flint. Hans Tralau (1974) labelled flint from Gotland "Ordovician flint" and suggested that it originates from submarine Ordovician layers north of Gotland. This leaves us with the questions:

• What kinds of flint can be found on Gotland?

- How does it compare visually and chemically to the Ordovician flint from Öland?
- Can we identify the source(s) of the flint nodules on Gotland?

Flint from Gotland, visual characterization

During a few hours' work we collected 27 flint nodules, 25 from a beach at Ihre and two from a beach at Nyhamn on Gotland. The nodules are small, ranging from the size of a squash ball to fist-sized. Most are rounded, like most of the other stones found on these beaches (fig. 2). Based on appearance, we could distinguish two types.

The visual variety we encountered most frequently (n=24) has a homogeneous grey matrix containing patches of coarser flint. It has a coarse texture and matte reflectivity, and the flaked surface is gritty and scaly. When a thin flake is held against a light source it is opaque. It has a white or yellowish weathered limestone cortex. The flint is easy to knap, though nodule size affects knappability (fig. 3). In the sections that follow we refer to this type as grey flint from Gotland (GF).

We encountered fewer nodules of the other type of flint (n=3, all from Ihre). This type has areas of both white and brown colour, with neither colour dominating. The matrix is homogeneous and the flint has a fine texture with matte reflectivity. The flaked surface is smooth. When a thin flake is held against a light source it is opaque. The cortex is grey and weathered. The flint is easy to knap, though nodule size may affect knappability (fig. 4). We call this type *white/brown* flint from Gotland (W/BF).

The two flint types we found on Gotland are visually distinct and it seems unlikely that they would originate from the same geological formation. It is also obvious that the flint from Gotland



Fig. 2. The beach at Ihre, north-west Gotland, and a close-up of a grey flint nodule (GF) with a yellowish weathered cortex found on the beach. The nodule is c. 5 cm long.



Fig. 3. Grey flint from Gotland (GF). The left-hand flake shows a yellowish brown patination on the unflaked ventral surface. The two other flakes show patination along the edges on the flaked dorsal surface. The right-hand flake is c. 5 cm long.

described here is visually distinctive from Ordovician flint from Öland.

Chemical analysis of flint samples from Gotland and Öland

Using the same instrument analysis protocol applied in previous work (Hughes et al. 2010, 2012), ten samples from Gotland (GF, n=9; and W/BF, n=1) and five samples of Ordovician flint from Öland, not previously examined, were analysed using non-destructive energy dispersive X-ray



Fig. 4. Flakes of white/brown flint (W/BF) from nodules found on the beach at Ihre, Gotland. The upper right flake is c. 4 cm long.

fluorescence (EDXRF) spectrometry. Fig. 5 plots six samples from Öland. These are the five analysed here, marked with blue triangles, plus one previously analysed sample, marked with an inverted green triangle. The laboratory analysis conditions and instrumentation used in the present study have been described elsewhere and those interested in such analytical detail may consult our most recent studies (Hughes et al. 2012; Högberg et al. 2013; 2014). All samples were cleaned with distilled water to remove any noticeable

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Sample name	Sample #Run #		Al2O2		Si	SiO2		SO3		Cl	
			%	error	%	error	%	error	ppm	error	
Gotland (Ihre)	ıA	1	0,928	0,03	89,5	0,1	0,02	0,001	242	8	
		2	0,943	0,03	89,38	0,1	0,029	0,001	295	8	
Gotland (Ihre)	2A	1	0,965	0,03	92,21	0,11	0,035	0,001	242	7	
		2	0,931	0,03	92,11	0,1	0,019	0,001	245	7	
Gotland (Ihre)	зA	1	1,76	0.03	88.21	0.11	0.061	0.001	361	0	
)	2	1,83	0,03	87,97	0,1	0,066	0,001	387	9	
			, ,	, ,						-	
Gotland (Ihre)	4A	1	1,07	0,03	92,96	0,1	0,028	0,001	303	7	
		2	1,09	0,03	93,24	0,1	0,025	0,001	328	7	
Cotland (Ihra)	- 1		a = (9		a a (⁹		6	10	
Gottand (mre)	54	1	0,74	0,03	°5,43	0,1	0,048	0,001	017	10	
		2	0,744	0,03	05,22	0,1	0,05	0,001	443	9	
Gotland (Ihre)	6A	1	1,06	0,03	94.09	0,11	0,030	0,001	297	7	
()		2	1,16	0,03	93,5	0,1	0,04	0,001	325	7	
Gotland (Ihre)	7A	1	1,61	0,03	86,4	0,1	0,037	0,001	287	8	
		2	1,63	0,04	86,79	0,1	0,039	0,001	286	8	
Castlen d (Thur)	0.4			-						_	
Gottand (Inre)	δA	1	0	0	99,54	0,1	0,029	0,001	427	7	
		2	0	0	99,19	0,1	0,032	0,001	090	9	
Gotland (Ihre)	9A	1	0,85	0,05	94,91	0,11	0,039	0,001	262	7	
· · · · ·	<i>,</i>	2	0,95	0,04	94,96	0,1	0,033	0,001	244	, 7	
Gotland (Nyham	n) 10A	1	0,84	0,03	93,1	0,1	0,048	0,001	261	7	
		2	0,98	0,05	92,03	0,11	0,038	0,001	278	7	
Öland	2	1	0 451	0.02	06.22	0.1	0.02	0.001	108	7	
olulid	2	2	0.504	0.03	90,22	0,1	0.028	0.001	271	7	
Öland	3	1	0,437	0.03	98,17	0,1	0,03	0,001	773	9	
	,	2	0.615	0.03	94.06	0.1	0.02	0.001	451	0	
Öland	4	1	0.180	0.03	98.46	0.1	0.016	0.001	246	8	
		2	0.104	0.03	98.71	0.1	0.01	0.001	43	7	
Öland	5a	1	0.575	0.03	08.37	0.1	0.023	0.001	371	7	
0 millio	Ju	2	0.626	0.02	08 21	0.1	0.02	0.001	218	7	
Öland	sh	1	0.624	0.02	90,31	0.1	0,02	0,001	527	10	
Oluliu	90	2	0,700	0.02	97,52	0.1	0.126	0.001	582	10	
		2	0,709	0,0,	97,12	0,1	0,120	0,001	J°,	10	
ICh-1(2/4/15)		2	0.211	0.02	08.82	0.1	0.002	0.001	0	0	
ICh-1(2/4/15)		1	0.212	0.02	08.80	0,1	0.002	0.001	0	0	
$ICh-1(6/16/1\epsilon)$		1	0.204	0.02	08.04	0.1	0,003	0.001	° °	0	
ICh-1(6/22/15)		1	0 272	0.02	08 75	0.1	0,003	0.001	° °	0	
JCh-1(6/24/15)		- 1	0,29	0,03	98,8	0,1	0,003	0,001	0	0	
JCh-1 (recommer	nded)		0,734		97,81	*	nr			14	
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Table 1. Quantitative composition estimates for geological flint samples from Gotland and Öland. Recommended values for standard JCh-1 from Imai et al. 1996.

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K2O		С	CaO		i	N	Mn		Fe	
%	error	%	error	ppm	error	ppm	error	ppm	error	
								11		
0	0	8,41	0,04	856	39	128	6	4948	24	
0,043	0,03	8,45	0,04	762	39	135	6	5028	25	
0,18	0,02	5,27	0,03	784	35	94	5	5433	24	
0,138	0,02	5,4	0,03	679	35	95	5	4766	22	
0,333	0,03	7,6	0,04	1235	42	109	6	9057	37	
0,358	0,03	7,66	0,04	1295	51	118	6	9025	37	
0,212	0,02	4,3	0,02	622	34	51	4	6156	26	
0,248	0,02	3,86	0,02	740	29	50	4	6330	26	
								(0		
0	0	12,54	0,05	731	43	140	7	5083	29	
0	0	12,71	0,05	700	43	133	7	5774	29	
				- 1 9		120	-			
0,349	0,02	3	0,02	718	33	139	5	5024	24	
0,204	0,02	3,45	0,02	759	33	132	>	50/2	24	
0.160	0.02	0.88	0.04	1128	52	170	7	8001	26	
0,171	0.02	9,00	0.04	1150	50	108	7	7880	25	
0,1/1	0,0,5	9137	0,04	1100	<u> </u>	190	/	7009	<u>,</u> ,	
0.088	0.02	0.070	0.02	03	8	0	1	267	5	
0.055	0.01	0,123	0.01	00	8	5	1	250	4	
-) -))	-) -	-) -)	-) -			,				
0,247	0,02	2,86	0,02	601	28	89	4	4382	19	
0,277	0,02	2,73	0,02	587	28	96	4	4268	19	
			,			<i>,</i>	-	-	<i>,</i>	
0,151	0,02	4,86	0,02	826	38	58	5	4852	22	
0,205	0,024	5,68	0,028	805	40	108	5	5292	24	
0,082	0,02	2,29	0,02	271	24	21	3	4925	20	
0,142	0,02	1,23	0,01	264	18	23	3	4805	20	
0,086	0,01	0,802	0,01	145	14	43	4	801	8	
0,022	0,02	4,483	0,02	447	26	335	6	2970	15	
0,19	0,01	0,193	0,01	178	14	12	2	3952	10	
0,154	0,01	0,171	0,01	198	13	15	2	3371	14	
0,337	0,01	0,074	0,01	380	15	10	2	3092	13	
0,348	0,01	0,085	0,01	370	10	12	2	3091	13	
0,3	0,01	0,21	0,01	900	40	17	3	4101	10	
0,340	0,01	0,208	0,01	928	50	15	3	4204	10	
0 225	0.01	0.026	0.002	206	18	120	4	2780	12	
0.22	0.01	0,030	0.02	180	17	127	4	2789	±5 12	
0.222	0.01	0.026	0.01	109	18	12/	7 4	2800	13	
0,201	0,01	0.028	0,01	101	18	124	4	2786	13	
0,227	0,01	0,037	0,01	180	18	120	4	2807	13	
,/	,-	-) -)1	,					/	,	
0,221		0,045		189		134		2490		
		, 19		/				.,		

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Fig. 5. CaO vs. Fe composition of flint samples from Gotland and Öland. Data for other Scandinavian flint types from Hughes et al. 2012. Plots for grey Gotland flint samples (red triangle) and white/brown flint Gotland sample (red triangle with white dot) were averaged from two separate EDXRF analyses (tab. 1). Data for Öland samples marked with blue triangles are the ones analysed here. Data for the Öland sample marked with an inverted green triangle come from Hughes et al. 2012, tab. 4. Note that at the scale used in the figure, the CaO/Fe composition of a sample from Öland appears to overlap with a single specimen from Kinnekulle, but the CaO figure for Kinnekulle (Hughes et al. 2012, tab. 4) is considerably higher than for these Öland samples.

surface contaminants. Care was taken to avoid targeting the X-ray beam onto calcareous or fossil inclusions. The only other requirement was that each sample be relatively flat, >15-20 mm in diameter, and have a minimum surface size for analysis of >2-3 mm. Data generated from the analysis of these 15 samples appear in tab. 1.

CaO vs. Fe data in tab. 1, plotted in fig. 5, show that the grey flint from Gotland (GF) is distinct in chemical composition from other types of Scandinavian flint. The difference mainly consists of greater iron and calcium concentrations. Compared to previous published data for Scandinavian flint (Hughes et al. 2012), flint from Poland (Högberg et al. 2013) and flint from Helgoland and northern Germany (Högberg et al. 2014), the chemical signature data for the grey Gotland flint is unique. In contrast, the CaO and Fe data from the white/brown flint type (W/BF), marked with a red triangle with a white dot, plot near

several south Scandinavian flint types (Högberg et al. 2012, fig. 5). While this result is provocative, it rests on a single sample. Further analyses based on more extensive sampling are needed in order to determine which of the Scandinavian types it is closest to in chemical composition.

Figs 5-6 show that the chemical compositions of flint from Öland and Gotland differ. Fig. 5 also shows that the chemistry of the samples from Öland can vary. A possible explanation for this variability might be that not all the samples from Öland are of Ordovician age.

Trace-element intensities for elements well measured by non-destructive EDXRF yielded values barely above, or below, detection limits for the majority of geological specimens we examined from mainland Scandinavia. They are thus of little use in distinguishing among those flints. In the present study, however, certain trace element measurements (e.g. Rb and Sr) were well

Fig. 6. Results from chemical analysis of flint samples from Gotland plotted using Sr and Rb. The Gotland flint plotting in the lower left in the figure is W/BF, the rest of the Gotland samples are grey flint. Values for Öland correspond to the samples marked with blue triangles in fig. 5. The sample marked with an inverted green triangle in fig. 5 is not included here.



above detection limits, so they are presented graphically in fig. 6. It shows that, although they are largely distinct on the basis of Rb vs. Sr traceelement abundances, some of the samples of grey flint from Gotland plot within the range measured for Öland samples. One possibility is that these few samples from Öland come from the same original geological source as the grey flint from Gotland, a source not known to us.

Conclusion

The CaO/Fe composition of grey flint from Gotland (GF) is unique in comparison with all other types of flint from Scandinavia, Poland and Germany analysed in previous studies. As for white/ brown flint from Gotland (W/BF), chemical analysis of one sample showed it to be similar to other types of Scandinavian flint analysed in our previous studies.

Our analysis shows that grey flint from Gotland is distinct from flint from Öland. It has different macroscopic properties and a different chemical composition. Hence, grey flint from Gotland is another type of flint. However, a single piece of flint from Öland that we analysed in a previous study (Hughes et al. 2012, tab. 4; plotted as an inverted green triangle in fig. 5) shows superficial chemical resemblance to the grey flint from Gotland, although it has much lower SiO2. We are not confident about the exact provenance of this specimen, so we hesitate to speculate further on its significance at this time.

Our results do not support Tralau's 1974 suggestion that Gotland beach flint might originate from submarine Ordovician layers north of the island. The CaO vs. Fe composition of our single sample of white/brown flint plots close to other types of Scandinavian flint that we have previously analysed. The chemistry of the grey flint nodules however is unlike that of any geological samples analysed to date from Scandinavia (Hughes et al. 2012), Poland (Högberg et al. 2013), Helgoland and northern Germany (Högberg et al. 2014) or from Lithuania and Belarus (Hughes et al. 2011).

If we have interpreted the geology of Gotland correctly, the flint nodules we sampled do not originate in the island's bedrock. Another source, or sources, must have contributed the small flint nodules we found. Future research can hopefully help us identify this source or sources. Given the known wide-ranging transport of Stone Age tools in the Baltic region (Martinsson-Wallin et al. 2011; Olausson et al. 2012) this knowledge might contribute to identifying locally produced tools, or tools produced on Gotland and found in assemblages from other areas around the Baltic.

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