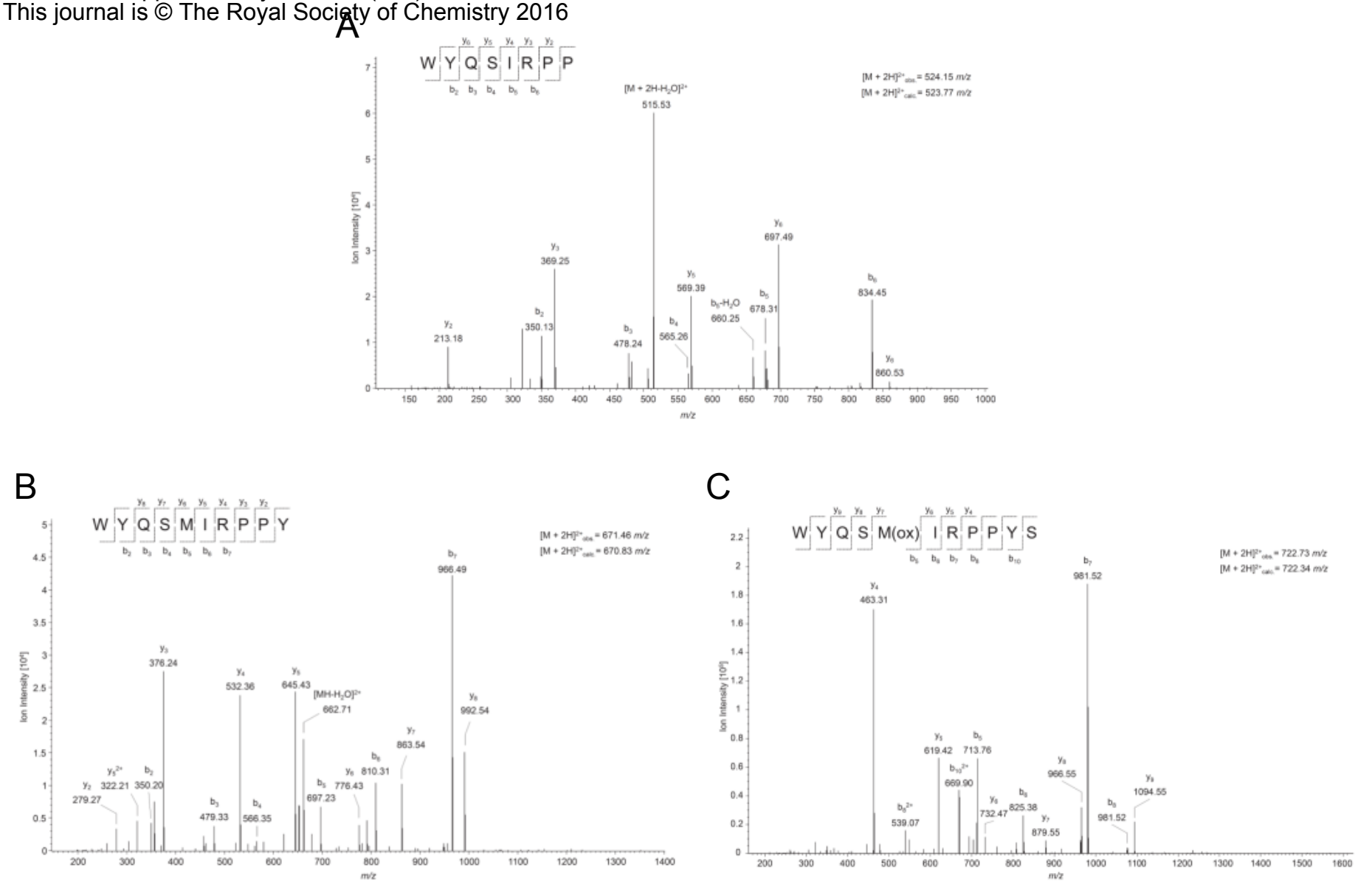
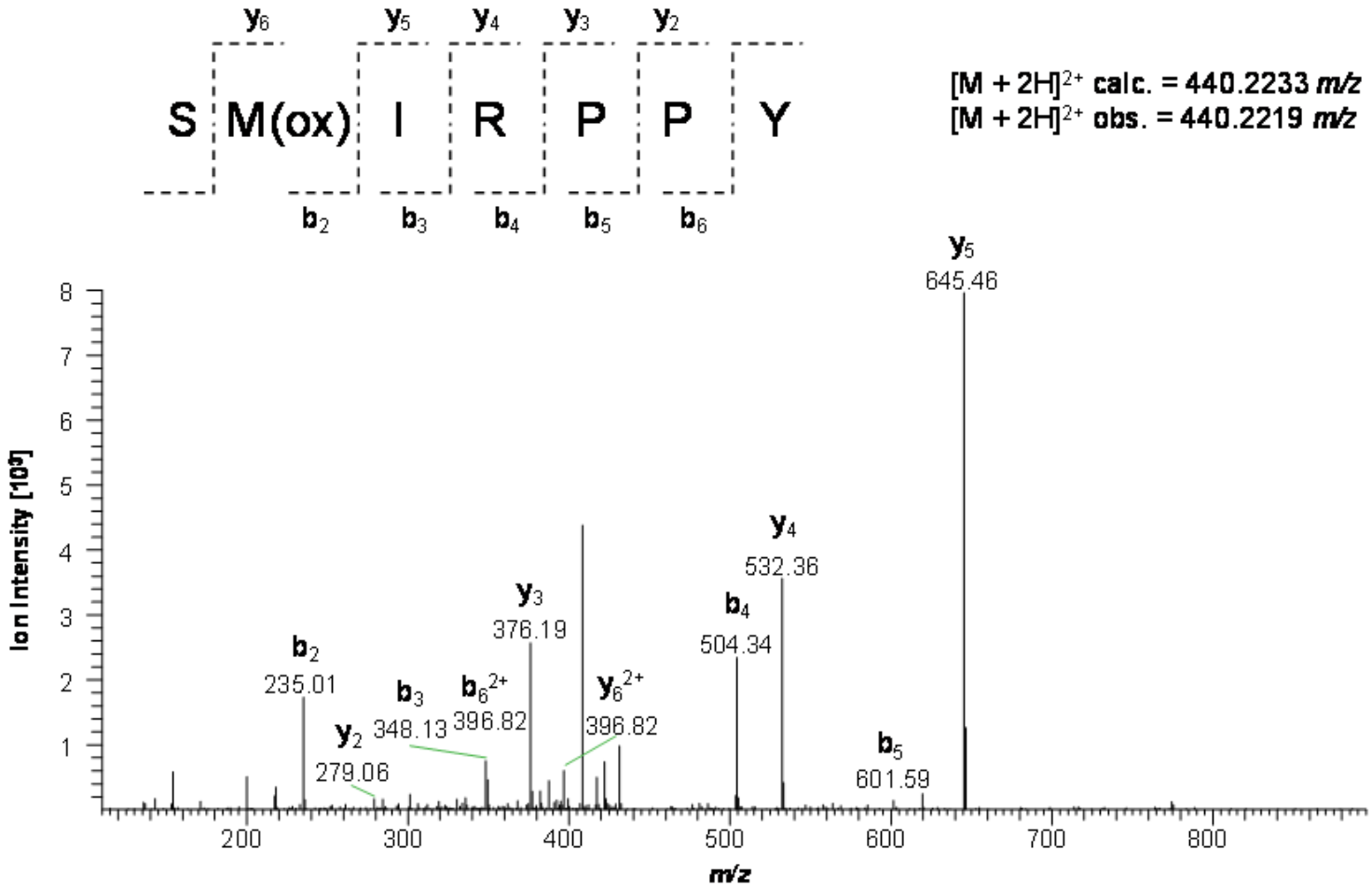
Electronic Supplementary Material (ESI) for RSC Advances.

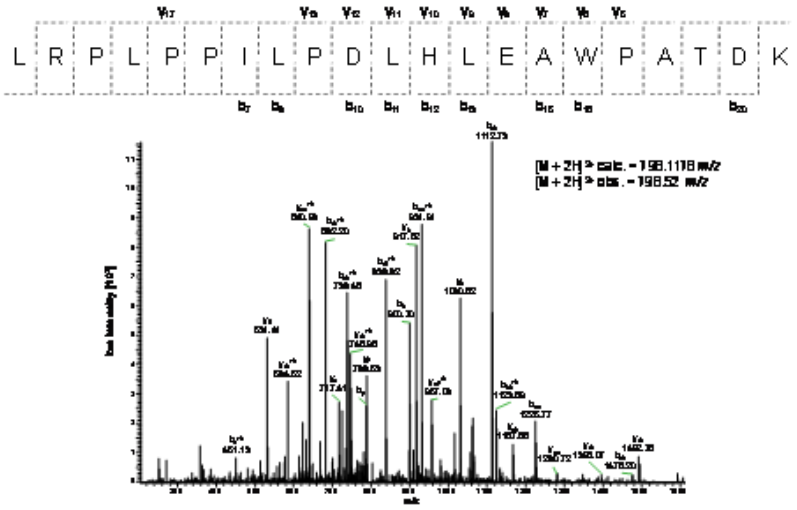


Supplementary Figure 1



Supplementary Figure 2

A



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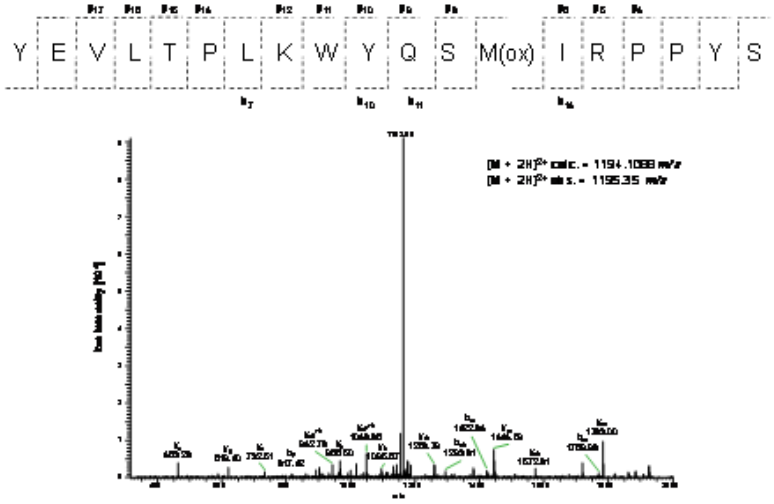
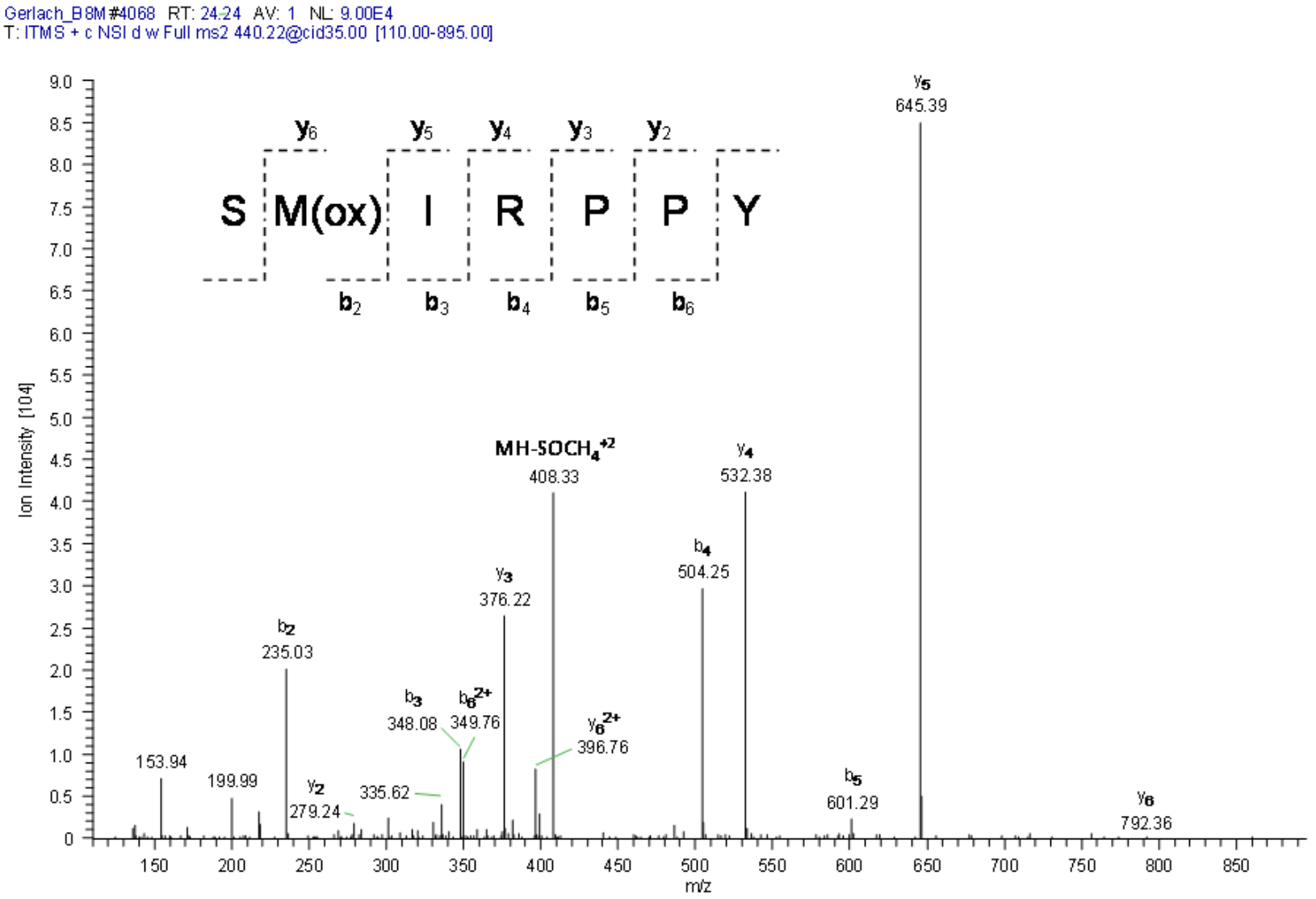


Supplementary Figure 3



Supplementary Figure 4

Supplementary Table 1

Sequence	Count	Amelogenin Isoforms
MPLPPHPG	1	Q99217;Q99217-3;Q99218;Q99218-1
MPLPPHPGHPG	2	
M(ox)PLPPHPGHPG	2	
MPLPPHPGHPGYIN	1	
M(ox)PLPPHPGHPGYINF	4	
LPPHPGHPG	1	
LPPHPGHPGY	2	
LPPHPGHPGYIN	1	
LPPHPGHPGYINF	11	
LPPHPGHPGYINFSYEVLTPLK	2	
MPLPPHPGHPGYINFSYEVLTPLK	2	
M(ox)PLPPHPGHPGYINFSYEVLTPLK	2	
PLPPHPGHPG	1	
PPHPGHPGYINF	1	
PHPGHPGYINF	3	
INFSYEVLTPLK	1	Q99217;Q99218-1
FSYEVLTPLK	1	
SYEVLTPLK	3	
SYEVLTPLKWYQ	1	
SYEVLTPLKWYQSIRPPYP	1	
YEVLTPLK	2	
YEVLTPLKW	1	
YEVLTPLKWYQ	1	
YEVLTPLKWYQS	1	
YEVLTPLKWYQSIRPPYP	6	
PLKWYQSIRPPYP	2	Q99217;Q99217-2;Q99217-3
LTPLKWYQSIRPPYP	1	
TPLKWYQSIRPPYP	4	
WYQSIRPP	1	
WYQSIRPPYP	1	
WYQSIRPPYPS	3	
WYQSIRPPYPSY	2	
WYQSIRPPYPSYG	2	
WYQSIRPPYPSYGYEP	1	
WYQSIRPPYPSYGYEPM(ox)G	2	
WYQSIRPPYPSYGYEPMGGW	2	
WYQSIRPPYPSYGYEPM(ox)GGW	3	
SIRPPYPSY	2	
SIRPPYPSYGYEPMGGW	3	
SIRPPYPSYGYEPM(ox)GGW	1	
MQPLPPMLPDLTLEAWPSTDK	1	
PPM(ox)LPDLTLEAWPSTDK	1	
LPDLTLEAWPSTDKTKREEVD	1	
DLTLEAWPSTDK	5	
LEAWPSTDKTKREEVD	1	
EAWPSTDKTKREEVD	1	
PSTDKTKREEVD	1	
ILFACLLGAAFAMPVLTPLKWYQSIRPPYP	2	Q99217-2
YEVLTPLKWYQSM(ox)IRPPYS	1	Q99218;Q99218-1
WYQSMIRPPY	1	
WYQSM(ox)IRPPY	1	
WYQSM(ox)IRPPYS	1	
LRPLPPILPDLHLEAWPATDK	2	

Supplementary Table 2

Sequence	Count	Amelogenin Isoforms
MPLPPHPG	2	Q99217;Q99217-3;Q99218;Q99218-1
M(ox)PLPPHPG	1	
MPLPPHPGH	2	
M(ox)PLPPHPGH	1	
MPLPPHPGHP	3	
MPLPPHPGHPG	5	
M(ox)PLPPHPGHPG	4	
M(ox)PLPPHPGHPGY	1	
MPLPPHPGHPGYIN	4	
M(ox)PLPPHPGHPGYIN	5	
MPLPPHPGHPGYINF	8	
M(ox)PLPPHPGHPGYINF	9	
LPPHPGHP	1	
LPPHPGHPG	6	
LPPHPGHPGY	1	
LPPHPGHPGYIN	3	
LPPHPGHPGYINF	21	
PHPGHPGYINF	7	
PLPPHPGHPG	1	
PPHPGHPGYINF	3	
SYEVLTPLK	5	Q99217;Q99218-1
SYEVLTPLKW	2	
YEVLTPLK	1	
YEVLTPLKW	2	
YEVLTPLKWY	2	
YEVLTPLKWYQ	4	
SIRPPYPSY	5	Q99217;Q99217-2;Q99217-3
SIRPPYPSYG	1	
SIRPPYPSYGYEP	2	
SIRPPYPSYGYEPM	2	
SIRPPYPSYGYEPM(ox)	2	
SIRPPYPSYGYEPMG	2	
SIRPPYPSYGYEPM(ox)G	3	
IRPPYPSY	1	
IRPPYPSYGYEPMG	1	
AWPSTDKTKREEVD	1	
PSTDKTKREEVD	1	
SM(ox)IRPPY	1	Q99218;Q99218-1

- **Appendices (Supplemental Data)**
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- **Supplementary Table 1.** Peptide sequences identified from amelogenin isoforms from first set of samples (with reductive alkylation and trypsin digest step). Peptides from isoform Y of amelogenin are shown in bold
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- **Supplementary Table 2.** Peptide sequences identified from amelogenin isoforms from second set of samples (simple acid etch). Peptide from isoform Y of amelogenin is shown in bold
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- **Supplementary Table 3.** Peptide sequences identified from amelogenin isoforms from c. 600 -900 AD samples (simple acid etch)
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- **Supplementary Figure 1.** Characteristic CID MS/MS spectra of the dimorphic peptides from isoforms X and Y of amelogenin: **A.** WYQSIRPP (from female sample, $[M+2H]^{2+}$ = 524.15 *m/z*), **B.** the oxidized form of the WYQSM(ox)IRPPYS (from male sample $[M+2H]^{2+}$ = 722.73 *m/z*) and **C.** WYQSMIRPPY peptide (from another male sample, $[M+2H]^{2+}$ = 671.46 *m/z*)
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- **Supplementary Figure 2.** CID MS/MS spectrum of the oxidized peptide from isoform Y of amelogenin: SM(ox)IRPPY (from male sample, $[M+2H]^{2+}$ = 440.2219 *m/z* recorded in orbitrap)
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- **Supplementary Figure 3.** CID MS/MS spectra of two additional dimorphic peptides from isoform Y of amelogenin identified from male samples: **A.** LRPLPPILPDLHLEAWPATDK and **B.** YEVLTPLKWYQSM(ox)IRPPYS
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- **Supplementary Figure 4.** CID MS/MS spectrum of the oxidized peptide from isoform Y of amelogenin: SM(ox)IRPPY from archaeological male sample, $[M+2H]^{2+}$ = 440.2230 *m/z* recorded in orbitrap)