F BRAY<sup>†</sup>, S FLAMENT

Univ. Lille, CNRS, USR 3290 - MSAP - Miniaturisation pour la Synthèse, l'Analyse et la Protéomique, F-59000 Lille, France

### G ABRAMS

Espace muséal d'Andenne, Rue Charles Lapierre 29, 5300, Sclayn, Belgium Faculty of Archaeology, Leiden University, Van Steenis Building, Einsteinweg 2, 2333 CC Leiden, The Netherlands

### D BONJEAN

Espace muséal d'Andenne, Rue Charles Lapierre 29, 5300, Sclayn, Belgium Department of Prehistory, University of Liège, Place du XX Août 7, 4000, Liège, Belgium

#### C ROLANDO

Univ. Lille, CNRS, USR 3290 - MSAP - Miniaturisation pour la Synthèse, l'Analyse et la Protéomique, F-59000 Lille, France Shrieking Sixties, 1-3 Allée Lavoisier, 59650 Villeneuve-d'Ascq, France

## C TOKARSKI

University of Bordeaux, Proteome Platform, 146 rue Leo Saignat, F-33076 Bordeaux, France

#### P AUGUSTE

Univ. Lille, CNRS, UMR 8198 - Evo-Eco-Paléo, Unité Evolution, Ecologie et Paléontologie, F-59000 Lille, France

<sup>†</sup>Corresponding author: <u>fabrice.bray@univ-lille.fr</u>

Table S5.1 Peptides and amino acids variations identified in the studied archaeological samples

*Figure S5.1 – S5.54: MS/MS spectra of peptides with amino acids variations.* 

Table S5.1 Peptides and amino acids variations identified in the studied archaeological samples. For each sample, the following information is described: peptides sequences, mass over charges (m/z), charge of peptides (z), the position and the type of mutation, the collagen chain, accession number and species. The peptides sequences are referencing the identified modifications (oxidation, deamidation, substitution). A m/z increase of +15.9949 corresponds to the oxidation of proline m/z increase + 0.9840 to deamidation of asparagine (N) or glutamine (Q). (sub \*) denotes the substitution of amino acid where \* is amino acid.

Samples	Peptide	m/z	Z	Position of mutation	Mutation	Protein	Accession number	Species
	N(sub G)EAGPSGPAGPTGAR	669.8234	2	779	$G \rightarrow N$	COL1A1	XP_042771858.1	Panthera leo
	GEQ(sub A)GPSGPAGPTGAR	669.8234	2	781	$A \rightarrow Q$	COL1A1	XP_042771858.1	Panthera leo
	GEAGPSGPAGPTGAE(sub R)GAP(+15.99)GDR	912.4112	2	793	$R \rightarrow E$	COL1A1	XP_042771858.1	Panthera leo
	N(sub G)PAGPAGPIGPVGAR	665.8649	2	1067	$\mathbf{G} \rightarrow \mathbf{N}$	COL1A1	XP_042771858.1	Panthera leo
	GPTGDP(+15.99)GKN(+.98)GDKGD(sub H)AGLAGAR	482.7312	4	513	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_042773912.1	Panthera leo
Sc-1	TN(sub G)ETGASGPP(+15.99)GFAGEK	768.3517	2	833	$\mathbf{G} \rightarrow \mathbf{N}$	COL1A2	XP_042773912.1	Panthera leo
Sc-2	TGEG(sub T)GASGPP(+15.99)GFAGEK	717.8282	2	835	$T \to G$	COL1A2	XP_042773912.1	Panthera leo
Sc-3	N(sub G)PSGAVGAP(+15.99)GVNGAP(+15.99)GEAGR	884.4193	2	908	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	XP_042773912.1	Panthera leo
	D(sub H)GN(+.98)RGEP(+15.99)GPAGVVGPVGAVGPR	678.3462	3	976	$\mathrm{H} \mathop{\rightarrow} \mathrm{G}$	COL1A2	XP_042773912.1	Panthera leo
	D(sub G)N(+15.99)RGEP(+15.99)GPAGVVGPVGAVGPR	996.0010	2	977	$\mathrm{G} \to \mathrm{D}$	COL1A2	XP_042773912.1	Panthera leo
	N(sub G)PTGPQGIR	470.2547	2	998	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	XP_042773912.1	Panthera leo
	TGD(sub H)PGSVGPAGVR	585.2981	2	1071	$\mathrm{H} {\rightarrow} \mathrm{D}$	COL1A2	XP_042773912.1	Panthera leo
	GDAGPD(sub P)GPAGPTGPP(+15.99)GPIGN(+.98)VGAP(+15.99)GPK	1171.059	2	838	$P \rightarrow D$	COL1A1	XP_019271349.1	Panthera pardus
	N(+.98)GDE(sub R)GETGPAGPAGPIGPVGAR	989.4691	2	1063	$R \rightarrow E$	COL1A1	XP_019271349.1	Panthera pardus

Sc-4	GEAGPSGPAGPTGAE(sub R)GAP(+15.99)GDR	912.4112	2	793	$R \rightarrow E$	COL1A1	XP_019271349.1	Panthera pardus
	GPTGDP(+15.99)GKN(+.98)GDKGD(sub H)AGLAGAR	482.7312	4	513	$\mathrm{H} \mathop{\rightarrow} \mathrm{D}$	COL1A2	XP_019298882.1	Panthera pardus
	N(sub G)DAGPP(+15.99)GPAGPTGPP(+15.99)GPIGN(+.98)VGAPGPK	794.3891	3	833	$\mathbf{G} \rightarrow \mathbf{N}$	COL1A1	XP_026368914.1	Ursus arctos horribilis
	AGEE(sub K)GHAGLAGAR	399.1977	3	511	$K \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	AGEKGD(sub H)AGLAGAR	586.8037	2	513	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	N(sub G)ETGAHGPP(+15.99)GFAGEK	495.5627	3	833	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	TGETGQ(sub A)HGPP(+15.99)GFAGEK	529.2446	3	837	$A \rightarrow Q$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	N(sub G)PP(+15.99)GAVGAP(+15.99)GVNGAP(+15.99)GEAGR	896.9307	2	908	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
Sc-5	N(+.98)IGPVGAVGAP(+15.99)GPD(sub H)GPVGPTG	644.3332	3	967	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	GN(+.98)IGPVGAVGAP(+15.99)GPD(sub H)GPVGPTGK	689.3215	3	967	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPVGAVGPR	668.6663	3	976	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	D(sub G)N(+15.99)RGEP(+15.99)GPAGAVGPVGAVGPR	981.4858	2	977	$\mathrm{G} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	GPSGPQ(+.98)GVRGDE(sub K)GEP(+15.99)GDKGPR	689.3215	3	1009	$K \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	IGG(sub H)P(+15.99)GTVGPAGVR	577.3196	2	1071	$\mathrm{H} \rightarrow \mathrm{G}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
Sc-6	N(sub G)DAGPP(+15.99)GPAGPTGPP(+15.99)GPIGNVGAP(+15.99)GP(+15.99)K	1205.582	2	833	$\mathbf{G} \rightarrow \mathbf{N}$	COL1A1	XP_026368914.1	Ursus arctos horribilis
	N(sub G)ESGNKGEP(+15.99)GSVGPQGPP(+15.99)GPSGEEGK	1241.0632	2	356	$\mathbf{G} \rightarrow \mathbf{N}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	Q(sub A)GEK(+15.99)GHAGLAGAR	635.3124	2	508	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	N(sub G)ETGLRGDVGNP(+15.99)GR	486.5744	3	659	$\mathbf{G} \rightarrow \mathbf{N}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	GEND(sub G)PVGPTGPVGSAGPSGPN(+.98)GPP(+15.99)GPAGSR	886.7492	3	758	$\mathrm{G} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis

	TN(sub G)ETGAHGPP(+15.99)GFAGEK	793.8668	2	833	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	N(sub G)PP(+15.99)GAVGAP(+15.99)GVN(+.98)GAP(+15.99)GEAGR	897.9244	2	908	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPVGAVGPR	502.0032	4	977	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	AGEE(sub K)GHAGLAGAR	399.1975	3	511	$K \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis
	AGEKGD(sub H)AGLAGAR	586.8041	2	513	$\mathrm{H} \mathop{\rightarrow} \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
0.7	GM(sub E)NGPVGPTGPVGSAGPSGPN(+.98)GPN(sub P)GPAGSR	1302.1116	2	722	$M \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis
SC-7				750	$P \rightarrow N$			
	TGEG(sub T)GAHGPPGY(sub F)AGEK	742.8411	2	835	$\mathrm{G} \rightarrow \mathrm{T}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
				843	$F \rightarrow Y$			
	NGDKGD(sub H)AGIAGPR	409.8735	3	1415	$S \rightarrow D$	COL1A2	Welker et al 2015	Mammuthus sp.
Sc-8	N(sub G)EVGPAGPNGFAGPAGAAGQ(+.98)AGAK	689.6691	3	1661	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	Welker et al 2015	Mammuthus sp.
	N(sub G)PP(+15.99)GPAGITGPP(+15.99)GPP(+15.99)GAAGK	879.4454	2	1692	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	Welker et al 2015	Mammuthus sp.
	GSAGPD(sub P)GATGFP(+15.99)GAAGR	731.3383	2	870	$P \rightarrow D$	COL1A1	NP_001029211.1	Bos primigenius taurus
Sc-9	GGP(+15.99)GSE(sub R)GFP(+15.99)GADGVAGPK	794.8610	2	492	$R \rightarrow E$	COL1A1	NP_001029211.1	Bos primigenius taurus
	GFP(+15.99)GADGVAGPE(sub K)GPAGER	828.8846	2	537	$K \rightarrow E$	COL1A1	NP_001029211.1	Bos primigenius taurus
	N(sub G)PP(+15.99)GESGAAGPTGPIGSR	819.3964	2	590	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	NP_776945.1	Bos primigenius taurus
	D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPAGAVGPR	988.4811	2	973	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	NP_776945.1	Bos primigenius taurus
	N(sub G)DAGPP(+15.99)GPAGPTGPP(+15.99)GPIGNVGAP(+15.99)GPK	1197.592	2	833	$G \square N$	COL1A1	XP_026368914.1	Ursus arctos horribilis
Sc-10	RGPN(+.98)GEAGSAGPSGPP(+15.99)GLE(sub R)GSP(+15.99)GSR	761.0187	3	400	$R \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis

AGEE(sub K)GHAGLAGAR	399.1973	3	511	$K \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis
N(sub G)PP(+15.99)GAVGAP(+15.99)GVNGAP(+15.99)GEAGR	896.9321	2	908	$\mathrm{G} \rightarrow \mathrm{N}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPVGAVGPR	501.7508	4	976	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
D(sub G)NRGEP(+15.99)GPAGAVGPVGAVGPR	649.3326	3	977	$\mathrm{G} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis
GPSGPQ(+.98)GVRGDE(sub K)GEP(+15.99)GDKGPR	689.6580	3	1009	$K \rightarrow E$	COL1A2	XP_026361636.1	Ursus arctos horribilis
IGD(sub H)P(+15.99)GTVGPAGVR	577.3197	2	1071	$\mathrm{H} \rightarrow \mathrm{D}$	COL1A2	XP_026361636.1	Ursus arctos horribilis





Figure S5.1. MS/MS spectrum of collagen COL1A1 from *Panthera leo*. The peptide of sequence N(sub G)EAGPSGPAGPTGAR at m/z 669.8254, z = 2 has a mutation at position 779.



Figure S5.2. MS/MS spectrum of collagen COL1A1 from *Panthera leo*. The peptide of sequence GEQ(sub A)GPSGPAGPTGAR at m/z 669.8234, z = 2 has a mutation at position 781.



Figure S5.3. MS/MS spectrum of collagen COL1A1 from *Panthera leo*. The peptide of sequence GEAGPSGPAGPTGAE(sub R)GAPGDR at m/z 912.4084, z = 2 has a mutation at position 793.



Figure S5.4. MS/MS spectrum of collagen COL1A1 from *Panthera leo*. The peptide of sequence N(sub G)PAGPAGPIGPVGAR at m/z 665.8654, z = 2 has a mutation at position 1067.



Figure S5.5. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence GPTGDP(+15.99)GKN(+.98)GDKGD(sub H)AGLAGAR at m/z 482.7312, z = 4 has a mutation at position 513, an oxidation on proline and a deamidation on asparagine.



Figure S5.6. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence TN(sub G)ETGASGPP(+15.99)GFAGEK at m/z 768.3517, z = 2 has a mutation at position 833 and an oxidation on proline.



Figure S5.7. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence TGEG(sub T)GASGPP(+15.99)GFAGEK at m/z 717.8282, z = 2 has a mutation at position 835 and an oxidation on proline.



Figure S5.8. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence N(sub G)PSGAVGAP(+15.99)GVNGAP(+15.99)GEAGR at m/z 884.4193, z = 2 has a mutation at position 908 and 2 oxidations on prolines.



Figure S5.9. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence D(sub H)GN(+.98)RGEP(+15.99)GPAGVVGPVGAVGPR at *m/z* 678.3462, *z* = 3 has a mutation at position 976, an oxidation on proline and a deamidation on asparagine.



Figure S5.10. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence D(sub G)N(+15.99)RGEP(+15.99)GPAGVVGPVGAVGPR at *m/z* 996.0010, *z* = 2 has a mutation at position 977 and 2 oxidations on proline and asparagine.



Figure S5.11. MS/MS spectrum of collagen COL1A2 from *Panthera leo*. The peptide of sequence N(sub G)PTGPQGIR at m/z 482.7312, z = 2 has a mutation at position 998.



Figure S5.12. MS/MS spectrum of collagen COL1A2 from *Panthera leo* The peptide of sequence TGD(sub H)PGSVGPAGVR at m/z 585.2981, z = 2 has a mutation at position 1071.



Figure S5.13. MS/MS spectrum of collagen COL1A1 from *Panthera pardus*. The peptide of sequence GDAGPD(sub P)GPAGPTGPP(+15.99)GPIGN(+.98)VGAP(+15.99)GP(+15.99)K at m/z 1178.5537, z = 2 has a mutation at position 838, 3 oxidations on proline and a deamidation on asparagine.



Figure S5.14. MS/MS spectrum of collagen COL1A1 from *Panthera pardus*. The peptide of sequence N(+.98)GDE(sub R)GETGPAGPAGPIGPVGAR at m/z 989.4691, z = 2 has a mutation at position 1063 and a deamidation on asparagine.

MS/MS spectra of peptides with mutation for sample Sc-5



Figure S5.15. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence AGEE(sub K)GHAGLAGAR at m/z 399.1977, z = 3 has a mutation at position 511.



Figure S5.16. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)ETGAHGPP(+15.99)GFAGEK at m/z 495.5627, z = 3 has a mutation at position 833, one oxidation on proline.



Figure S5.17. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence AGEKGD(sub H)AGLAGAR at m/z 586.8037, z = 2 has a mutation at position 513.



Figure S5.18. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)ETGAHGPP(+15.99)GFAGEK at m/z 495.5627, z = 3 has a mutation at position 833 and an oxidation of proline.



Figure S5.19. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence TGETGQ(sub A)HGPP(+15.99)GFAGEK at m/z 529.2446, z = 3 has a mutation at position 837 and an oxidation of proline.



Figure S5.20. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)PP(+15.99)GAVGAP(+15.99)GVNGAP(+15.99)GEAGR at m/z 896.9307, z = 2 has a mutation at position 908 and 3 oxidations on prolines.



Figure S5.21. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(+.98)IGPVGAVGAP(+15.99)GPD(sub H)GPVGPTGK at m/z 644.3332, z = 3 has a mutation at position 967, an oxidation on proline and a deamidation on asparagine.



Figure S5.22. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence GN(+.98)IGPVGAVGAP(+15.99)GPD(sub H)GPVGPTGK at *m/z* 689.3215, *z* = 3 has a mutation at position 967, an oxidation on proline and a deamidation on asparagine.



Figure S5.23. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPVGAVGPR at m/z 668.6663, z = 3 has a mutation at position 976, an oxidation on proline and a deamidation on asparagine.



Figure S5.24. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence D(sub G)N(+15.99)RGEP(+15.99)GPAGAVGPVGAVGPR at m/z 981.4858, z = 2 has a mutation at position 977 and an oxidation on proline and an oxidation on asparagine.



Figure S5.25. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence GPSGPQ(+.98)GVRGDE(sub K)GEP(+15.99)GDKGPR at m/z 689.3215, z = 3 has a mutation at position 1009, an oxidation on proline and a deamidation on glutamine.



Figure S5.26. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence IGG(sub H)P(+15.99)GTVGPAGVR at m/z 577.3196, z = 2 has a mutation at position 1071 and an oxidation on proline.

MS/MS spectra of peptides with mutation for sample Sc-6



Figure S5.27. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)ESGNKGEP(+15.99)GSVGPQGPP(+15.99)GPSGEEGK at m/z 1241.0632, z = 2 has a mutation at position 356 and 2 oxidations on prolines.



Figure S5.28. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence Q(sub A)GEK(+15.99)GHAGLAGAR at m/z 635.3124, z = 2 has a mutation at position 508 and an oxidation on proline.



Figure S5.29. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)ETGLRGDVGNP(+15.99)GR at m/z 486.5744, z = 3 has a mutation at position 659 and an oxidation on proline.



Figure S5.30. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence GEND(sub G)PVGPTGPVGSAGPSGPN(+.98)GPP(+15.99)GPAGSR at m/z 886.7492, z = 3 has a mutation at position 752 with an oxidation on proline and a deamidation on asparagine.



Figure S5.31. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence TN(sub G)ETGAHGPP(+15.99)GFAGEK at m/z 793.8668, z = 2 has a mutation at position 833 with an oxidation on proline.



Figure S5.32. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)PP(+15.99)GAVGAP(+15.99)GVN(+.98)GAP(+15.99)GEAGR at m/z 897.9244, z = 2 has a mutation at position 908 with 2 oxidation on prolines and a deamidation on asparagine.



Figure S5.33. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPVGAVGPR at m/z 502.0032, z = 4 has a mutation at position 976 with an oxidation on proline and a deamidation on asparagine.

MS/MS spectra of peptides with mutation for sample Sc-7



Figure S5.34. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence AGEE(sub K)GHAGLAGAR at m/z 399.1975, z = 3 has a mutation at position 511



Figure S5.35. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence AGEKGD(sub H)AGLAGAR at m/z 586.8041, z = 2 has a mutation at position 513



Figure S5.36. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence GM(sub E)NGPVGPTGPVGSAGPSGPN(+.98)GPN(sub P)GPAGSR at m/z 1302.1116, z = 2 has mutations at position 750 and 772



Figure S5.37. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence TGEG(sub T)GAHGPPGY(sub F)AGEK at m/z 742.8411, z = 2 has mutations at position 835 and 843.

MS/MS spectra of peptides with mutation for sample Sc-8



Figure S5.38. MS/MS spectrum of collagen COL1A2 from *Mammuthus sp*. The peptide of sequence NGDKGD(sub H)AGIAGPR at m/z 409.8735, z = 3 has a mutation at position 1415.



Figure S5.39. MS/MS spectrum of collagen COL1A2 from *Mammuthus sp*. The peptide of sequence N(sub G)EVGPAGPNGFAGPAGAAGQ(+.98)AGAK at m/z 689.6691, z = 3 has a mutation at position 1611, and 1 deamidation on glutamine.



Figure S5.40. MS/MS spectrum of collagen COL1A2 from *Mammuthus sp*. The peptide of sequence N(sub G)PP(+15.99)GPAGITGPP(+15.99)GPP(+15.99)GAAGK.E at m/z 879.4454, z = 2 has a mutation at position 1692, and 3 oxidations on proline.

MS/MS spectra of peptides with mutation for sample Sc-9



Figure S5.41. MS/MS spectrum of collagen COL1A1 from *Bos primigenius taurus*. The peptide of sequence GGP(+15.99)GSE(sub R)GFP(+15.99)GADGVAGPK at m/z 794.861, z = 2 has a mutation at position 492 and 2 oxidation on prolines.



Figure S5.42. MS/MS spectrum of collagen COL1A1 from *Bos primigenius taurus*. The peptide of sequence GSAGPD(sub P)GATGFP(+15.99)GAAGR at m/z 731.3385, z = 3 has a mutation at position 870 and an oxidation on proline.



Figure S5.43. MS/MS spectrum of collagen COL1A1 from *Bos primigenius taurus*. The peptide of sequence GFP(+15.99)GADGVAGPE(sub K)GPAGER at m/z 828.8846, z = 2 has a mutation at position 537 and an oxidation on proline.



Figure S5.44. MS/MS spectrum of collagen COL1A1 from *Bos primigenius taurus*. The peptide of sequence GSP(+15.99)GEAGR(+15.99)PGEAGLP(+15.99)GAE(sub K)GLTGSP(+15.99)GSP(+15.99)GPDGK at*m*/*z*966.1173,*z*= 3 has a mutation at position 537 and 4 oxidations on prolines and arginine.



Figure S5.45. MS/MS spectrum of collagen COL1A2 from *Bos primigenius taurus*. The peptide of sequence N(sub G)PP(+15.99)GESGAAGPTGPIGSR at m/z 819.3964, z = 2 has a mutation at position 590 and an oxidation on proline.



Figure S5.46. MS/MS spectrum of collagen COL1A2 from *Bos primigenius taurus*. The peptide of sequence D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPAGAVGPR at m/z 988.4811, z = 2 has a mutation at position 973 with an oxidation on proline and a deamidation on asparagine.

MS/MS spectra of peptides with mutation for sample Sc-10



Figure S5.47. MS/MS spectrum of collagen COL1A1 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)DAGPP(+15.99)GPAGPTGPP(+15.99)GPIGNVGAP(+15.99)GPK at m/z 1197.5920, z = 2 has a mutation at position 833 and 3 oxidations on prolines.



Figure S5.48. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence RGPN(+.98)GEAGSAGPSGPP(+15.99)GLE(sub R)GSP(+15.99)GSR at m/z 761.0187, z = 3 has a mutation at position 400, 2 oxidations on prolines and a deamidation on asparagine.



Figure S5.49. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence AGEE(sub K)GHAGLAGAR at m/z 399.1973, z = 3 has a mutation at position 511.



Figure S5.50. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence N(sub G)PP(+15.99)GAVGAP(+15.99)GVNGAP(+15.99)GEAGR at m/z 896.9321, z = 2 has a mutation at position 908 and 3 oxidations on prolines.



Figure S5.51. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence D(sub H)GN(+.98)RGEP(+15.99)GPAGAVGPVGAVGPR at m/z 501.7508, z = 4 has a mutation at position 976, an oxidation on proline and an deamidation on asparagine.



Figure S5.52. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence D(sub G)NRGEP(+15.99)GPAGAVGPVGAVGPR at m/z 649.3326, z = 3 has a mutation at position 977, an oxidation on proline.



Figure S5.53. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence GPSGPQ(+.98)GVRGDE(sub K)GEP(+15.99)GDKGPR at m/z 689.6580, z = 3 has a mutation at position 1009, an oxidation on proline and a deamidation on glutamine.



Figure S5.54. MS/MS spectrum of collagen COL1A2 from *Ursus arctos horribilis*. The peptide of sequence R.IGG(sub H)P(+15.99)GTVGPAGVR.G at m/z 577.3197, z= 2 has a mutation at position 1071 and an oxidation on proline.