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Characterisation of metallic mordants in Subarctic Athapaskan quillwork: a PIXE-RBS study on replicate samples

Caractérisation de mordants métalliques dans des ornements en piquants de porc-épic (culture Athapaskan subarctique) : une étude PIXE-RBS sur des échantillons re-créés en laboratoire

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Fig. 1. Bracelet of tanned caribou skin decorated with porcupine quills and blue beads, Athapaskans (Acc. N°: A.849.6). © National Museums Scotland/Photography Neil McLean.

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Abstract. *Native American quillwork collections remain little studied due to the limited availability of quillwork material for sampling. In this paper we explore the use of non-invasive Particle Induced X-Ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) to characterise metallic residues in a set of modern porcupine quills prepared with a range of metallic mordants. PIXE analysis was used to determine the concentrations of various mordants present, while RBS analysis allowed additional information on the depth-profiling of the mordants at the surface of the quills to be obtained.*

Keywords. *Quillwork, porcupine quills, dyeing practices, metallic mordants, Northern Athapaskans, PIXE analysis, RBS analysis.*

Résumé. *Les collections nord-amérindiennes décorées avec la technique de la teinture des piquants de porc-épic restent très peu étudiées, en raison de la difficulté de prélever ce type de collections. Dans cet article, nous explorons l'utilisation de l'analyse par faisceau d'ions (PIXE-RBS) pour la caractérisation de résidus métalliques sur des piquants de porc-épic de référence préparés en laboratoire avec différents mordants. L'analyse PIXE nous a permis de caractériser les concentrations de mordants métalliques présents à la surface des piquants de porc-épic, tandis que l'analyse par rétrodiffusion de Rutherford (RBS) nous a permis d'obtenir des informations complémentaires sur la répartition de ces mordants dans les couches superficielles de la kératine.*

Mots-clés. *Travail aux piquants, piquants de porc-épic, teinture, mordançage, Athapaskan du Nord, analyse PIXE, analyse RBS.*

Introduction

Indigenous communities across North America, from the North American Subarctic, Great Lakes region and the Northern Plains, have long used dyed porcupine quills and goose quills to decorate garments and basketry (fig. 1). Clothing was a very important aspect of First Nations culture; clothes and footwear were manufactured from tanned caribou hides and were adapted to the climate of the Subarctic. These clothes were decorated with sophisticated embroidery using dyed porcupine quills (but also moose hair or goose quills) and fringing[1]. Northern Athapaskan[2] artefacts in particular are very rare, with significant collections including those of the Canadian Museum of Civilization and National Museums Scotland (NMS), the latter having the oldest and most extensive collection of 19th century Dene artefacts in the world today[3].

In comparison to textile collections[4], quillwork collections have received little systematic study and only limited information is available about the actual dye sources[5] and dyeing processes used by native North Americans[6]. Earlier research suggested that only native dyes were used for quillwork dyeing without mordant, but our recent study of a group of dyed porcupine quills and objects collected in 1862[7] from Northern Athapaskans (fig. 2) revealed that non-native dye sources (natural and semi-synthetic) were also used in combination with several metallic mordants (Fe, Cu and Sn)[8].

It is known that dyeing with the majority of natural dyes requires treatment of the textile substrates with an aqueous solution of mordant, generally a metal salt of aluminium, copper or iron. There is however no equivalent information available for quillwork dyeing. Sources of aluminium include biological accumulators of aluminium, potash alum [$AlK(SO_4)_2 \bullet 12H_2O$], or ammonium alum [$Al_2(NH_4)_2(SO_4)_4 \bullet 12H_2O$]. Sources of iron include green copperas [$Fe(SO_4) \bullet 7H_2O$], iron sulfate [$Fe_2(SO_4)_3$] or iron oxide Fe_2O_3, while copper mordant was obtained from copper sulfate [$CuSO_4$] and tin mordant was prepared from the dissolution of pewter in concentrated nitric acid (aqua fortis) replaced later by tin salts [$SnCl_2$][9]. During this treatment the mordant is absorbed by the fibre and a mordant-fibre complex or dye-mordant-fibre is created (scheme 1)[10]. The choice of the mordant is important in the textile

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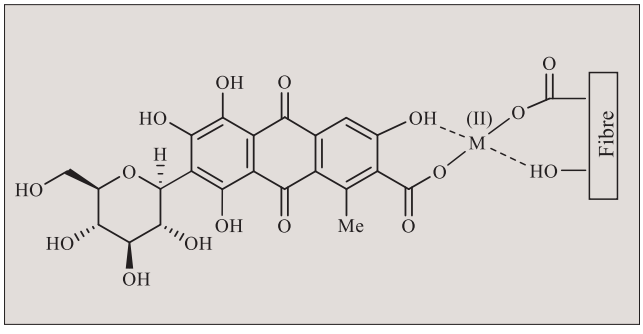
Fig. 2. Specimens of dyed porcupine quills collected in 1862 from Northern Athapaskans (Acc. N°: A.848.15), © National Museums Scotland/Photography Isabell Wagner.

preparation as it will affect greatly the final colour of the textile: for example the use of copper salts will darken the colour of the dye while in contrast the use of tin salts will brighten the colour.

Due to the difficulties in sampling quillwork for analysis, in this paper we explore the use of the highly sensitive techniques, non-invasive Particle Induced X-Ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) to characterise metallic residues in porcupine quillwork. Although PIXE and to a lesser extend RBS techniques are well established for the study of museum objects[11], their application to organic-based materials is much more limited[12]. In order to better understand the sorption of metallic mordants on porcupine quill substrates, we additionally analysed replicate porcupine quill reference samples prepared in house with a range of concentration of copper(II) and tin(II) ions.



Scheme 1. Example of complex formed during the dyeing processes between an anthraquinone dye molecule, a metallic mordant (M) and the side-chain groups of a proteinaceous fibre.

Materials and methods

Reference specimens

Porcupine quills (*Erethizon* sp.) purchased from Native American artist Sarah Tronti were scoured and then dyed with either (i) cochineal (*Dactylopius coccus* C.) purchased from DBH Ltd Poole England, or (ii) turmeric (*Curcuma longa* L.) purchased from George Weil & Sons Ltd. Mordants, including alum, copper(II) sulfate, tin(II) chloride, iron(II) sulfate, chromium(IV) oxide, and cream of tartar were purchased from George Weil & Sons Ltd. Typically, dry quills (0.3 g) were dyed in a solution containing dyestuff (33 wt.%) and metallic mordants (25 wt.% alum, or 5-6 wt.% otherwise) for 1 h at 85-90 °C, as is traditionally reported for wool dyeing[13]. Additionally, a set of porcupine quills were prepared by dyeing several quills (0.2 g) in a 50 mL dyebath containing cochineal dye (2.00 g) and variable amounts of copper(II) sulfate (> 99 %, Sigma Aldrich) and a second dyebath with variable amounts of tin(II) chloride (> 99 %, Sigma Aldrich) in order to obtain dyebath concentrations in Cu(II) or Sn(II) of 100; 500; 1000 and 2500 ppm.

Particle Induced X-Ray Emission and Rutherford Backscattered Spectrometry (PIXE/RBS)

Analyses were performed at the external beamline of the AGLAE facility with a 3 MeV proton beam and a final analytical spot size of 50 µm, two Si(Li) detectors for PIXE analysis (with 125 µm Be filter and 28.5 mm air for High Energy detector)[14]. Additional PIXE measurements were performed using a newly implemented detection system with two Peltier-cooled SDD detectors[15]. Simultaneous RBS analyses were performed using a charged particle detector in IBM

geometry[16], with a scattering angle of 150°. All measurements were undertaken in a He-rich atmosphere. In order to decrease, or avoid, a visible modification of the quill under the beam, a beam current of 3-6 pA was used and an area of 100 × 500 µm was scanned for an average of 4-5 minutes. Quantitative analysis was performed in trace mode using GUPIXWIN and TRAUPIXE software[17], modelling a thick layer of keratin using the elements C, H, N, O, S in proportion to their reported relative wt.%[18]. RBS spectra were simulated with SIMNRA software[19] taking into account non-Rutherford reactions for the light elements in keratin (C, N, O)[20].

Investigation of metallic residues in quillwork by PIXE-RBS techniques

PIXE analysis of modern replicate porcupine quills

Porcupine quills are made of hard α-keratin[21] and present a highly crystalline structure, with the external layer of the quill (cuticle) being less ordered compared to the internal layer of the quill[22]. Although there are extensive studies on the properties of wool and hair fibres, or feathers, especially with regard to their uptake of dyes and metal ions[23], there are only a very limited number of studies on porcupine quills and their dyeing properties[24].

In contrast to wool fibres, where the dyestuff is evenly distributed through the fibre, generally only the thin cuticle layer of quills interacts with the dyebath and adsorbs the dyestuffs and metal ions[25]. The thickness of this cuticle averages 60 µm, while the range of the 3 MeV protons PIXE beam has been evaluated as 136 µm for a matrix of keratin by TRIM software (SRIM 2003 version)[26]. The effective depth values have been calculated for a range of elements using the GUCSA module of GUPIX software and vary between a minimum of 52 µm for S(K_α) and a maximum of 80 µm for Hg(L_α). These effective depth values mean that the concentration of mordant determined by PIXE corresponds to the average value of mordant present in the cuticle layer, and in cases where the cuticle is thinner to the contribution of mordant present in both the cuticle and the cortex. The limit of detection (LoD) of each element was averaged from 50 to 70 measurements using GUPIX software[27] and calculated for both experimental set-ups. LoDs ranged between 3 ppm for Fe(K_α) and 60 ppm for Sn(L_α).

It is known that the uptake of metal ions on keratinous substrates is variable between ions[28] and depends on the treatment time and temperature, with longer heating times and higher temperatures giving rise to a substantial increase in the total uptake of metal ions by the substrates[29]. PIXE analysis of a small set of modern replicate quills prepared with dyebaths containing combinations of cream of tartar, alum, Cr, Fe, Cu and Sn showed that it was possible to differentiate the individual dyebath processes (table 1). It was found that the levels of S in modern replicate quills ranged between 2 and 4 wt.%, as would be expected in keratin. Traces of Zn were detected in all the modern replicate quills, including a scoured one, at an average concentration of 50 ppm.

In order to better understand the sorption of copper and tin onto porcupine quills, we additionally analysed quills prepared with various concentrations of Cu(II) and Sn(II) mordants. PIXE analysis showed that these replicate quills present significant heterogeneity both across the surface of any one individual quill and between individual quills; as a result multiple measurements taken on different quills prepared using the same dyebath conditions gave 20-25% variation in the values obtained for metal ion concentrations. Nevertheless, it is clear from these experiments that the uptake of Cu(II) and Sn(II) in the cuticle layer increases with increasing dyebath concentrations and that Sn(II) ions exhibit a higher affinity than Cu(II) ions for the quill substrate (fig. 3).

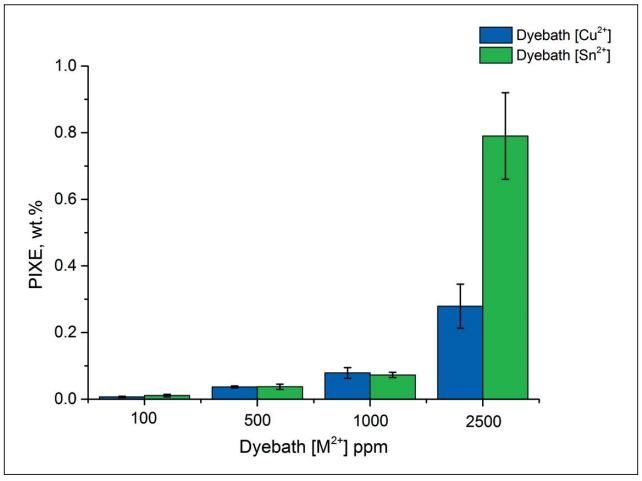


Fig. 3. Comparison of the sorption of Cu(II) and Sn(II) onto porcupine quills as measured by PIXE (wt.%) with varying dyebath concentrations of the metal ion (ppm). For each dyebath concentration, 4 to 5 measurements on multiple quills were undertaken by PIXE; data are presented as the mean of these measurements with error bars depicting one standard deviation of the variation in measurements.

It is known that Sn(IV) has a strong affinity for wool substrates[30], and is therefore likely, despite the different oxidation state, that Sn(II) would also have a high affinity for porcupine quill substrates. Furthermore, in the case of Sn(II), there is a distinct possibility that under the dyebath conditions used, some reaction could have occurred between the catechol unit of carminic acid and Sn(II) ions leading to the formation of a Sn(IV)-catechol ligand, as has been observed in other studies[31]. Finally, residual levels of S and Cl were observed in the replicate quills prepared with $CuSO_4$ and $SnCl_2$ respectively, with these levels increasing with increasing dyebath concentrations (table 1).

Table 1. PIXE elemental data obtained with the High Energy detector for a selection of modern quills. Entries marked "•" correspond to an average of 3 to 5 measurements from several quills prepared in the same dyebath conditions; PIXE analysis entries marked "¤" correspond to a level below LoD.

	PIXE										
Entry	***S*** *(wt.%)*	***Cl*** *(ppm)*	***K*** *(ppm)*	***Ca*** *(ppm)*	***Cr*** *(ppm)*	***Fe*** *(ppm)*	***Zn*** *(ppm)*	***As*** *(ppm)*	***Hg*** *(ppm)*	***Sn*** *(ppm)*	***Cu*** *(ppm)*
Modern replicate quills											
Scoured quill	2.8	836	–	350	–	10	68	¤	¤	¤	¤
Al, K, Cr	1.6	49	3944	379	1280	8	87	¤	¤	¤	5
Al, K, Sn	2.3	799	4173	702	¤	8	55	¤	¤	480	7
Cu	3.1	76	380	111	¤	¤	32	¤	¤	¤	224
K, Fe	4.0	4693	2460	109	¤	101	18	¤	¤	¤	¤
Cu, 100 ppm •	2.2	89	1984	796	–	7	48	–	–	–	70
Cu, 500 ppm •	2.3	207	1675	939	–	5	43	–	–	–	367
Cu, 1000 ppm •	3.4	268	303	756	–	8	27	–	–	–	794
Cu, 2500 ppm •	3.2	378	648	1201	–	6	44	–	–	–	2788
Sn, 100 ppm •	2.3	192	3502	618	–	12	49	–	–	109	–
Sn, 500 ppm •	2.0	1385	845	5536	–	4	45	–	–	373	6
Sn, 1000 ppm •	2.3	4018	2077	751	–	3	35	–	–	726	8
Sn, 2500 ppm (dyebath 1) •	1.3	11294	621	1108	–	3	23	–	–	7866	92

RBS analysis

The quills were simultaneously analysed by RBS which provided additional information on the depth-profiling of the mordant in the cuticle layer. For the majority of the samples a two-layered model was used for simulation with SIMNRA software, comprising a thin layer of keratin containing traces of heavy metals over an infinite layer of keratin (fig. 4a). The thickness of Layer 1 was evaluated to ~80 000 $\times 10^{15}$ Atoms cm^{-2} which is equivalent to 9 µm considering the atomic composition and density of keratin. This layer also presents a "roughness" of ~40 000 $\times 10^{15}$ Atoms cm^{-2}, which is equivalent to a gradient in composition (table 2). This model showed a good correlation for the RBS spectra obtained from scoured (fig. 4b) and mordanted modern quills (fig. 4c-d), Cu and Sn were observed in the RBS spectra of the reference quills for concentrations as low as 200-300 ppm (fig. 4c). However, it was not possible to differentiate the contribution of S and Cl elements in the SIMNRA simulation in the quills prepared with $SnCl_2$ due to their close kinematic factors (fig. 4d).

For all the samples, the composition of Layers 1 and 2 was found to closely match the expected atomic concentrations for keratin, with the addition of traces of mordant (table 2)[32]. However, in all the samples analysed it was observed that the level of S and mordant was found to be higher in Layer 1 (4 to 5 wt.% for S) than the average values determined by PIXE

	× 10^{15} Atoms cm^{-2}		**% Atomic Composition**						
	Thickness	**Roughness**	**C**	**H**	**O**	**S**	**N**	**Sn**	**Cu**
Scoured quills									
Layer 1	80000	40000	33.0	47.5	10.0	1.5	8.0	–	–
Layer 2	Infinite		33.0	44.3	13.0	0.7	9.0	–	–
Modern quills: Cu(II), 500 ppm									
Layer 1	60000	50000	33.0	45.2	12.0	0.7	9.0	–	0.07
Layer 2	Infinite		33.0	47.8	10.0	0.2	9.0	–	–
Modern quills: Sn(II), 2500 ppm (dyebath 1)									
Layer 1	45000	40000	33.0	43.2	13.0	1.5	9.0	0.3	–
Layer 2	Infinite		33.0	46.8	10.2	1.1	9.0	–	–

Table 2. % Atomic composition of the postulated layers in the SIMNRA simulation of: scoured modern replicate quills; modern replicate quills mordanted with $CuSO_4$ (500 ppm); modern replicate quills mordanted with $SnCl_2$ (2500 ppm).

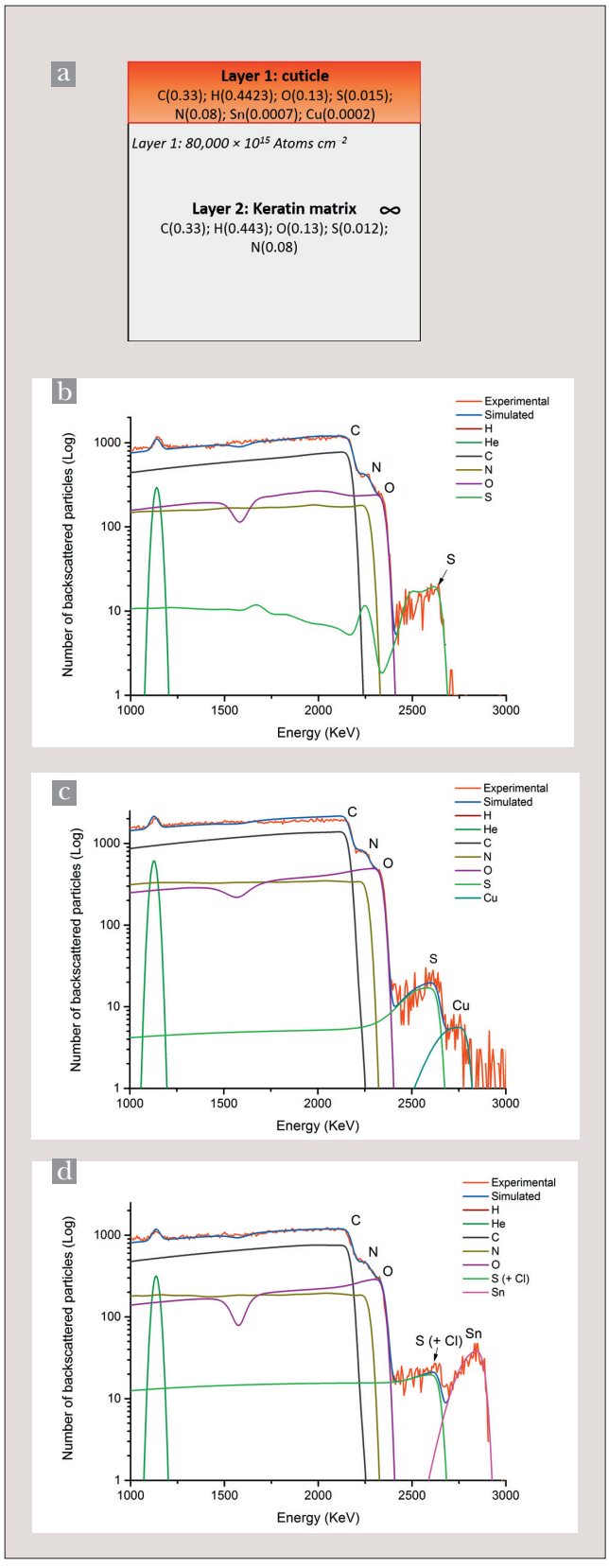


Fig 4. (a) Two-layered model used for SIMNRA simulation; with atomic compositions and layer thicknesses in Atoms cm^{-2} provided by the SIMNRA simulation; experimental and simulated RBS spectra obtained with a 3 MeV proton-beam on (b) a scoured modern quill, (c) a quill prepared with a 500 ppm $CuSO_4$ dyebath solution and (d) a quill prepared with 2500 ppm $SnCl_2$ dyebath solution.

(1.5 to 2.5 wt.% for S). While a higher level of S is expected in the outer cuticle[33], the higher levels of mordants could possibly correspond to a deposition on the surface of the cuticle.

Conclusion

The combination of PIXE and RBS analysis provides an alternative non-destructive methodology for the study of these keratin-based materials. While PIXE analysis allows the concentrations of various mordants (Fe, Cu, Sn) at the surface of the quills to be determined, RBS allows additional depth-profiling of the mordants at the surface of the quills to be obtained. The concentrations and distribution of metal ions have been determined on modern replicate porcupine quills prepared using known dyebath concentrations of these ions.

These results present a promising approach for the study of quillwork and related keratinous materials. Future investigation might focus on the analysis of modern replicate quills prepared with successive dyebaths containing either different mordant or dyestuff combinations to investigate the effects of overdyeing processes on the metal ion concentrations observed. From a methodological point of view, the results presented were obtained during the development of the new AGLAE multi-detector, before the automated imaging system was installed. Thus future study of these fragile materials should include PIXE and RBS mapping (which should soon be possible at the AGLAE), as well as analysis by total IBA technique.

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Notes

1. Thompson (1994), p. XIII-XVI and p. 3-20.

2. The term Athapaskan refers to both a cultural group and a language family, see Krauss and Golla (1981), p. 67-85. Athapaskans, also called "Dene" can be subdivided into three groups, Northern, Pacific Coast and Southern. Northern Athapaskans include the Tłıcho, the Gwich'in, the Slavey, and the Chypewyan, all living from the Hudson's Bay in the east to the interior of the Alaska coast in the west, Thompson (1990), p. 3-9.

3. For National Museums Scotland Athapaskan collection, see publications from Mc Fayden Clark and Idiens (1974), p. 13-43; Idiens (1979), p. 1-20; Knowles (2007), p. 37-56. Additional examples of Northern Athapaskan quillwork from the McKenzie River district (Bata Shoe Museum) may be found in Thompson (1990), *op. cit.* (note 2), p. 11-21.

4. A review of the dye sources used in European historical textile dyeing can be found in Ferreira *et al.* (2004), p. 329-336.

5. See Cole and Heald (2010), p. 1-6; Cole (2010), p. 102-160 for the investigation of dye sources in pre-1856 Eastern Woodlands quillwork; See Troalen (2013) p. 204-254; Troalen *et al.* (2016), p. 83-91 for dye sources in 1862 Athapaksan quillwork.

6. Orchard (1919), p. 6-8 and the recent review on the documentary sources describing quill dyeing techniques, Bohr and Lindsay (2009), p. 21-35; See additionally Troalen (2013) *op. cit.* (note 5) and Troalen *et al.* (2016) *op. cit.* (note 5).

7. The Athapaskan quill specimens from National Museums Scotland were previously described as "*natural, and some coloured in red and blue with European aniline dyes*", probably due to their bright colours. MacFayden Clark and Idiens (1974), *op. cit.* (note 3), p. 102.

8. Troalen (2013), *op. cit.* (note 5); Troalen *et al.* (2016), *op. cit.* (note 5).

9. Cardon and du Châtenet (1990), p. 21-24; Hofenk de Graaf (2005), p. 22-23 and Ferreira *et al.* (2004), *op. cit.* (note 4).

10. Ferreira *et al.* (2004), *op. cit.* (note 4).

11. Calligaro, Dran and Salomon (2004), p. 227-276; Beck *et al.* (2010), p. 2086-2091; Albéric *et al.* (2015), p. 100-108 p. 100-108.

12. Beck *et al.* (2012), p. 203-207.

13. Cardon and du Châtenet (1990), *op. cit.* (note 9).

14. Pichon *et al.* (2010), p. 2028-203.

15. Pichon *et al.* (2014), p. 27-31.

16. Pichon *et al.* (2010), *op. cit.* (note 14).

17. Campbell *et al.* (2010), p. 3356-3363; Pichon *et al.* (2010), *op. cit.* (note 14); Pichon *et al.* (2015), p. 45-54.

18. Masson (1963), p. 179-180; Zahn *et al.* (2000), p. 548-576.

19. Eckstein and Mayer (1999), p. 337-344.

20. Beck *et al.* (2012), *op. cit.* (note 12).

21. MacArthur (1943), p. 38-41; Fraser, McRae, Rogers (1972), p. 83-110.

22. Busson, Engström, Doucet (1999), p. 1021-1030.

23. Fergusson, Holzbecher, Ryan (1983), p. 121-135; Carr, Evans, Roberts (1987), p. 109-113; Suyama, Fukazawa, Suzumara (1996), p. 67-74; Kar and Misra (2004), p. 1313-1319.

24. Bohr and Lindsay (2009), *op. cit.* (note 6); Troalen (2013), *op. cit.* (note 5).

25. Troalen *et al.* (2016), *op. cit.* (note 5).

26. Biersack and Haggmark (1980), p. 257-269.

27. Campbell *et al.* (2010), *op. cit.* (note 18).

28. Fergusson, Holzbecher, Ryan (1983), *op. cit.* (note 23).

29. Suyama, Fukazawa, Suzumara (1996), *op. cit.* (note 23); Sheffield and Doyle (2005), p. 203-207.

30. Sakaguchi (1969), p. 1053-1055.

31. Wakley and Varga (1972), p. 169-178; Budesinsky (1972), p. 909-910; Hernández Méndez *et al.* (1987), p. 288-292.

32. Troalen *et al.* (2016), *op. cit.* (note 5).

33. Bradbury *et al.* (1966), p. 1333-1334.

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