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SCIENCE DIRECT
Applied Surface Science 252 (2006) 6582–6587
applied surface science
www.elsevier.com/locate/apsusc

Matrix-enhanced secondary ion mass spectrometry: The Alchemist's solution?

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Received 12 September 2005; accepted 15 February 2006
Available online 9 May 2006

Abstract

Because of the requirements of large molecule characterization and high-lateral resolution SIMS imaging, the possibility of improving molecular ion yields by the use of specific sample preparation procedures has recently generated a renewed interest in the static SIMS community. In comparison with polyatomic projectiles, however, signal enhancement by a matrix might appear to some as the alchemist's versus the scientist's solution to the current problems of organic SIMS. In this contribution, I would like to discuss critically the pros and cons of matrix-enhanced SIMS procedures, in the new framework that includes polyatomic ion bombardment. This discussion is based on a short review of the experimental and theoretical developments achieved in the last decade with respect to the three following approaches: (i) blending the analyte with a low-molecular weight organic matrix (MALDI-type preparation procedure); (ii) mixing alkali/noble metal salts with the analyte; (iii) evaporating a noble metal layer on the analyte sample surface (organic molecules, polymers).

Keywords: Organic SIMS; Imaging SIMS; Matrix; ME-SIMS; MALDI; MetA-SIMS; Metal; Salt; Cluster ion

1. Introduction

Traditionally in SIMS, the term 'matrix effects' has been used to describe the drastic influence of the chemical environment over the desorption/ionization yields of sputtered particles. Elements like oxygen and cesium have been found to enhance the yields of positive and negative ions, respectively, of other elements by several orders of magnitude. In organic SIMS, matrix and substrate effects are also very important, as was already demonstrated almost three decades ago [1]. Matrix effects constitute a huge obstacle for quantification. However, they present an excellent opportunity for secondary ion yield enhancement, especially at a time when the development of SIMS imaging, triggered by the outstanding focusing capabilities of liquid metal ion probes, requires much higher yields than those we are able to 'naturally' measure.

In this article, I consider a broad definition of the term ''matrix''. The ''matrix'' is any chemical species added to the analyte molecules during – or after – the preparation of the sample to increase their characteristic sputtered ion yield, without any constraint concerning the nature and the proportions of the additives, or the structure of the resulting sample (molecular-scale mixing, separate phases, crystallinity, etc.). The only restriction applies to the case of inorganic and metal substrates. Indeed, the literature involving the use of specific substrates for secondary ion enhancement and cationization in SIMS [2,3] is vast and addressing the state-of-the-art in that specific field would require a separate article. Note that, in contrast with inorganic substrates, the procedures discussed hereafter have the potential to be used for real-world sample analysis.

Matrices, according to the above definition, have undoubtedly proven to be beneficial for the analysis of large organic and biomolecules. In the late 1970s/early 1980s, Cooks and co-workers reported remarkable sensitivity increases and a certain control of the internal energy of molecular ions embedded in ammonium chloride [4] and demonstrated the advantage of using metal salts for molecule cationization/anionization [1]. More recent experiments have shown that peptides such as bovine ubiquitin (molecular weight, MW = 8565 Da) and even chicken egg lysozyme (MW = 14,305 Da) could be detected as intact molecules in the mass spectra after appropriate dilution in a selected matrix [5]. Despite these encouraging results and many others, the use of matrices for SIMS analysis never really

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doi:10.1016/j.apsusc.2006.02.076

took off, even though it literally exploded in the laser ablation literature, with the advent of matrix-assisted laser desorption ionization (MALDI) [6,7]. Perhaps the complexity and empirical nature of the procedure could have frightened a community more strongly rooted in energetic particle physics than chemistry (difficulty of finding the adequate matrix, the proper dilution, the best method to form the matrix:analyte mixture, inevitably leading to reproducibility problems). Perhaps SIMS was inherently less capable of taking over killer application fields such as genomics and proteomics, because of its more limited mass range. One may now wonder if matrix-enhanced SIMS still has a place in the new realm of organic SIMS, ruled by polyatomic projectiles, which has made the technique literally leap forward with respect to molecular ion sensitivity and 3-D analysis capabilities [8].

After a brief description of some important results related to the different procedures of matrix-enhancement, including not only their achievements but also their drawbacks, their relevance in the current context of SIMS will be discussed.

2. Molecules in a low-molecular weight organic matrix (matrix-enhanced SIMS)

The origin of the sample preparation procedure involving the dilution of the analyte in a low-MW organic matrix has been partly sketched in Section 1 (see Ref. [9] for a more detailed review). In this section, I focus on reports published in the last decade, starting when the method was reintroduced into the SIMS community by Wu and Odom [5], that is, after the breakthrough of MALDI. Since then, the method has evolved on various fronts. First, its applicability has been demonstrated for a panel of analytes including peptides, proteins, nucleic acids [5,10–13] in the range 1–15 kDa and also for other types of molecules such as phospholipids [14], organic dyes [15] and polymers [16]. Several matrices have been tested, some directly transposed from MALDI (2,5-dihydroxybenzoic acid – 2,5-DHB [5,12,14,15]; *a*-cyano-4-hydroxycinnamic acid – 4HCCA [5,10,11,15]; sinapinic acid [12,15]) and also others, such as nitrocellulose [13], frozen organic solvents [17], ice [18] and trehalose sugar [19]. However, it appears that more/different types of matrices could be tested, especially because SIMS is not submitted to the constraint of photon absorption that limits the number of efficient matrices in MALDI. In a slightly different line, analytes have also been deposited on/with molecular layers of cocaine and thiols [12,20–22]. A recent and exciting field of investigation concerns the chemical imaging of organic and biological samples [23,24], as exotic as freshwater snail (*Lymnaea stagnalis*) and cockroach (*Blaberus giganteus*) brains. For this purpose, the issue of low-lateral resolution resulting from the ''dried droplet'' sample preparation procedure [14] could be alleviated by electrospraying the matrix on the sample.

A representative example of the molecular yield enhancement induced by the use of a matrix is presented in Fig. 1 for the case of Chain B of insulin in a 4HCCA matrix [10]. The mass spectra show clear molecular ion peaks in both positive and

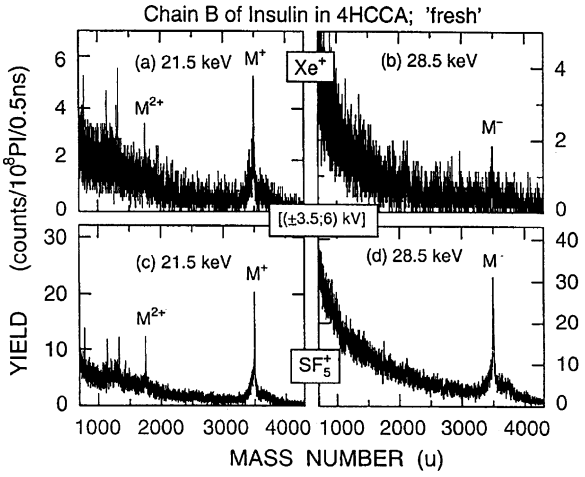

Fig. 1. (a–d) ME-SIMS. High-mass region of the positive and negative secondary ion mass spectra of Chain B of insulin in 4HCCA, bombarded with Xe^+ and SF_5^+. Reprinted with permission from Ref. [10]. Copyright Elsevier (2000).

negative ion polarities and for both Xe^+ and SF_5^+ ion bombardment conditions. Insulin molecular ions in general could not be observed on neat sample coatings cast, spin-cast or sprayed on silicon wafers [5,10]. Note that, for the same projectile fluences and kinetic energies, SF_5^+ provides significantly higher molecular ion intensities than Xe^+, an effect that will be recalled in Section 6. In addition, the fact that both protonated $(M + H)^+$ and deprotonated $(M - H)^-$ molecular ions are observed with high intensities suggests that several ionization pathways may be simultaneously favored by the presence of the matrix.

The mechanism of molecular ion yield enhancement resulting from the use of a low-MW organic matrix is multifacetted. The matrix has a strong influence on the analyte desorption process, as proposed by several authors [1,5,10] and further demonstrated by molecular dynamics (MD) studies involving polystyrene oligomers (PS-MW = 2 kDa) embedded in a trimethylbenzene matrix (TMB-MW = 120 Da) [9]. First, the matrix isolates the analyte molecules, thereby easing their extraction from the environment, usually hampered by molecular entanglement or crystallinity. Second, because of the low cohesive energy of the matrix:analyte medium, large numbers of molecules are sputtered per ion impact and the analyte appears to be 'naturally' entrained by the sputtered matrix molecule flux. In this respect, the fact that the molecule velocities are close to those observed in MALDI suggests an analogy of mechanisms between both irradiation regimes [9]. Third, large clusters of matrix molecules, with or without an analyte molecule, are observed among the ejected species in the simulations [9]. These clusters evaporate after emission, thereby lowering the internal energy of their constituents, which should favor the formation of 'cool' analyte molecules. Note that the collective entrainment of the analyte with the matrix also contributes to generate molecules with relatively low internal energies. The matrix strongly influences the ionization of the analyte molecules, too. The role of matrix molecules in the ionization process [24], for instance as proton donors [5,15], has been recognized in several experimental

studies. The question whether gas-phase (or selvedge) reactions, predominant in MALDI, play an important role in the SIMS ionization process, however, is still debated [10,15]. Finally, the observation of very large analyte-to-matrix yield ratios (up to 250 for protonated molecules [10]) suggests the possibility of analyte segregation at the extreme surface.

3. Molecules mixed with metal salts

As was the case for organic matrices, the genesis of the application of metal salts for improved ionization dates back to the early years of static SIMS [1,25]. Alkali and transition metal salts have been used by several research groups over the years, as an alternative to low-MW matrices or to promote the cationization of molecules that are difficult to ionize otherwise, such as non-polar and aromatic molecules [16,26–28]. Salts are routinely added to the usual sample preparation procedure for the MALDI analysis of synthetic polymers [29], a combination that has also been tested in SIMS with mixed results [16,28].

The ability of transition metal salts such as silver trifluoroacetate (AgTFA), copper acetylacetonate (CuACAC) and gold trichloride ($AuCl_3$) to promote the cationization of kilodalton molecules is illustrated in Fig. 2, for an Irganox

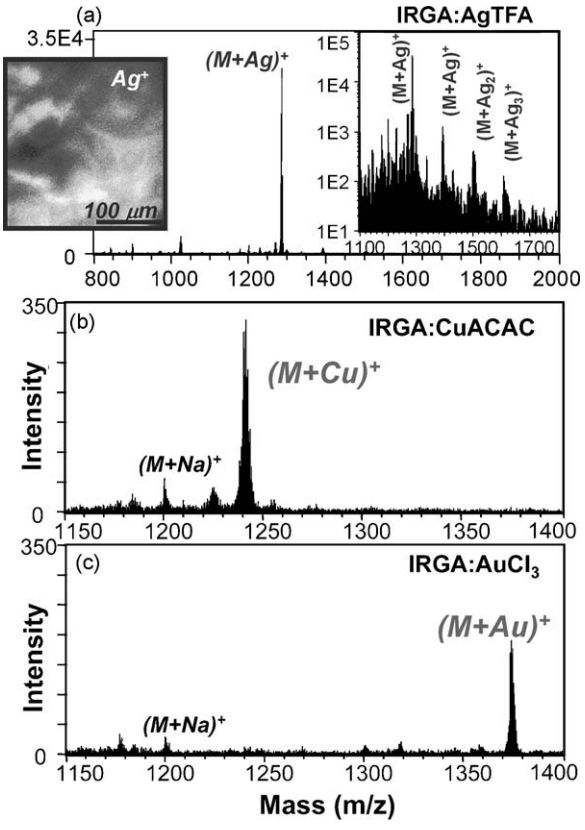

Fig. 2. Molecules mixed with transition metal salts. Positive secondary ion mass spectra of (a) Irganox 1010™ cast on silicon from a THF solution containing AgTFA salts. *Inset spectrum*: the same in a log scale showing the various adduct ions $(M + Ag_n)^+$. *Inset image*: chemical mapping of Ag^+ for a similar sample. (b) Irganox 1010™ cast from a CuACAC-containing solution; (c) Irganox 1010™ cast from a $AuCl_3$-containing solution. Adapted with permission from Ref. [28]. Copyright American Chemical Society (2005).

1010™ analyte (MW = 1076 Da, a polymer antioxidant) [28]. The case of AgTFA is particularly intriguing, first, because very high yields of quasimolecular ions are measured and, second, because silver cluster ions and larger adduct ions of the type $(M + Ag_n)^+$ are also present in the mass spectra. This observation indicates that the silver atoms form clusters on the sample surface.

The influence of metal salts on the dynamics of sputtering, if any, has not been elucidated. Concerning ionization, the results are in agreement with the hard and soft acids and bases (HSAB) concept, i.e. weak bases such as aromatic molecules are better cationized by weak acids (group Ib metal cations) [1,28] and hard bases such as peptides are more efficiently ionized by hard acids (alkali cations) [26,28]. In a more quantitative manner, the binding energies and structures of organic molecules attached to metal cations have been calculated by several authors [30–32].

4. Gold and silver evaporation on the molecular sample surface (metal-assisted SIMS)

Ironically enough, metal-assisted SIMS [33–37] uses gold and silver nanoparticles as the ''Philosopher's Stones'' to turn complex solid mixtures into their quintessential fractions, the cationized molecules. Noble metal clusters or nanoparticles naturally form at the surface of most organic and polymeric solids in the first stage of the physical vapor deposition (PVD) process, because of the unbalance between the forces binding metal atoms (stronger) and those binding them to the organic surface (weaker) [38,39]. Typically, a metal fluence under 50 nmoles/cm^2 gives rise to the formation of clusters [40], whose abundance and size depend on the nature of the metal and the sample [41,42]. Even though the cationization capabilities of metallization had been recognized earlier [43,44], the discovery of the beneficial effect of thin gold [33] and silver [45,46] cluster layers on the desorption/ionization of organic molecules is recent. In the last 3 years, the efficiency of MetA-SIMS has been demonstrated for a wide range of samples, encompassing low- [33,36] and high- [33,47] molecular weight polymers, polymer additives [33,34], peptides [34], pharmaceuticals, organic dyes [35] and paints [48]. A particularly interesting test case concerns the high-resolution imaging of biological tissues, namely, rat kidneys [37,49].

A typical result of the MetA-SIMS procedure is shown in Fig. 3. The sample is a dried droplet of a dilute PS solution on a biaxially stretched polypropylene (PP) film [34]. Twenty nmoles/cm^2 of gold were evaporated on the sample surface afterwards and the sample was analyzed in the following 2 h. The high mass range of the positive SIMS spectrum (Fig. 3a–b) shows a series of Au_n^+ clusters, a distribution of Au-cationized PP chain segments and a distribution of Au-cationized PS oligomers, which are due to the PS coating non-uniformity, as witnessed by the secondary ion images (Fig. 3c–f). None of these quasimolecular ions could be observed without pretreatment. In addition, the intensity of the characteristic PP and PS fragments such as $C_4H_9^+$ and $C_7H_7^+$ show a yield increase of one to two orders of magnitude with

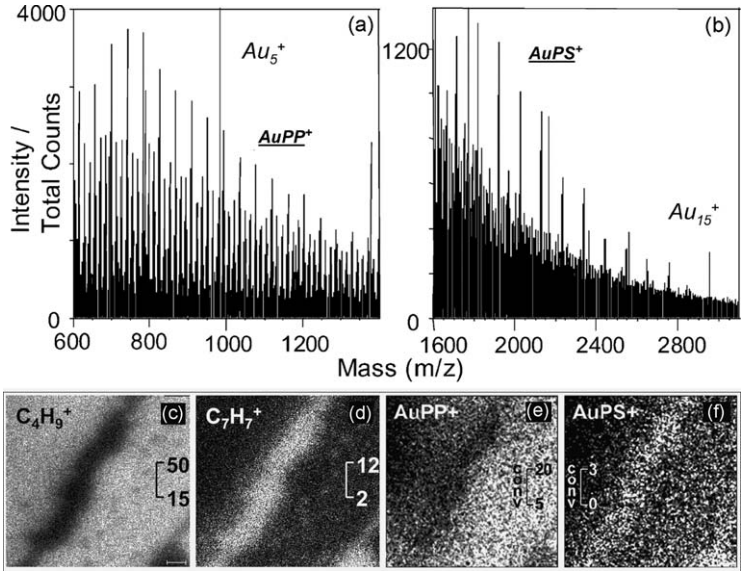

Fig. 3. MetA-SIMS. TOF-SIMS imaging on a polypropylene film locally covered by PS oligomers and metallized with Au (20 nmoles/cm^2). (a) Region of the mass spectrum showing the distribution of Au-cationized PP chain segments; (b) region of the mass spectrum showing the distribution of Au-cationized PS oligomers; (c–f) 120 μm × 120 μm images of (c) the butyl fragments of PP; (d) the $C_7H_7^+$ fragments of PS; (e) the Au-cationized chain segments of PP; (f) the Au-cationized PS oligomers. Adapted with permission from Ref. [34]. Copyright American Chemical Society (2003).

respect to untreated samples. As a result, SIMS images with much better signal-to-noise ratios are obtained after metallization. The procedure also suppresses the need for charge compensation.

The mode of action of metal clusters on the sputtering and ionization processes of organic molecules is still under investigation. Metallization creates/enhances several ionization pathways for molecules departing the surface, the most obvious being the cationization by a metal atom/ion [33,36,37]. The enhancement observed for bare fragment [34] and parent ions [34,35], both positive and negative [33], suggests other scenarios, probably related to the specifics of the electronic structure of the sample at the metal–organic frontier/interface. It should be mentioned that, for relatively short molecules (1 kDa or less), diffusion of the molecules over the metal clusters or islands in the time separating sample metallization from analysis is probable [34,35]. In this particular case, the enhancement effect is probably analogous to that observed with bulk metal substrates.

5. Comparative study

In this section, I compare the three aforementioned methods with respect to a series of criteria. The results of this comparison are summarized in Table 1. This table has been established on the basis of a personal interpretation of the information available in the literature and, therefore, it may neither reflect the cumulated experience/opinions of all the researchers in the field nor the very recent evolution of the techniques.

The following bullets provide comments and remarks about the table:

- *Efficiency:* The three procedures generate high yields of quasimolecular ions, though some reports question the performance of the salt procedure [15,16]. The comparison between ME-SIMS and MetA-SIMS indicates that the latter is generally more efficient for risperidone and organic dyes [15]. On the other hand, the mass range of the MetA-SIMS and salt procedures is more limited (∼3 kDa) [33].
- *Reproducibility/control:* ME-SIMS [11,12,14] and salt procedures [28] are particularly sensitive to parameter changes. One important issue concerns the variation in the matrix crystal size/structure [14].
- *Versatility:* MetA-SIMS is readily applicable to any kind of organic material (real-world samples), even though the question of sample heating upon metallization has been raised [24]. The salt procedure could benefit from electrospray deposition, such as ME-SIMS.
- *Ease of interpretation:* Organic matrices and possibly salts produce peak interferences in the low mass range of the SIMS spectra [15]. The metal ions in MetA-SIMS are easily separated from the analyte-related peaks [35].
- *Imaging capability:* Ultimately, the resolution limit of MetA-SIMS might be better than that of ME-SIMS, due to the smaller size of the metal clusters (∼20 nm) [40,41] with respect to the matrix crystals (∼1 μm) [23,24]. The

Table 1
Comparison of the different sample preparation procedures used for molecular ion signal enhancement in static SIMS

Criterion	ME-SIMS	Salt	MetA-SIMS
Efficiency	++	+ (++)	++
Reproducibility/control	−	−	+
Versatility	±	− (±)	++
Ease of interpretation	−	±	+
Imaging capability	+ (++)	?	++
Equipment/cost	+ (−)	+	−

(++) Very good; (+) good; (±) satisfactory; (−) limiting; (?) unknown.

performance of the salt procedure for imaging has not been evaluated yet.

- *Equipment/cost:* MetA-SIMS demands an evaporator [33,36] or a sputtering equipment [35–37]. ME-SIMS requires an electrospray apparatus to obtain small size, uniformly deposited matrix crystals [23,24].

6. Matrix-enhanced-SIMS and polyatomic projectile bombardment

Polyatomic projectiles such as Au_n^+ and C_{60}^+ bombarding bulk molecular samples give rise to molecular *ion* yields that can be, at times, up to four orders of magnitude larger than those measured upon Ga^+ bombardment and, in general, about two orders of magnitude larger [50–54]. For ice samples, the measured number of H_2O equivalents removed per projectile, i.e. the molecular *sputtering* yields, are 100 for Au^+, 1190 for Au_3^+ and 2510 for C_{60}^+ [55]. Such yield enhancements are remarkable and it is not clear that matrix-enhanced SIMS (in general) can always compete, except for specific cases. In addition, one may argue that state-of-the-art polyatomic ion sources, with their reliability, their current stability and their long lifetimes, overcome many of the problems encountered with matrix-enhanced SIMS. Even though these two very different approaches have not been directly compared yet, polyatomic projectiles seem to offer a more robust, elegant and global response to the issue of ion yield improvement in organic samples (the 'scientist's solution' mentioned in Abstract).

The situation, however, is not as clear as it appears. The many reports on polyatomic projectile bombardment indicate a strong variation of the observed yield enhancements as a function of the chosen projectile, the analyzed sample and the considered secondary ion (as a non-exhaustive list, see for instance [50,52,53]). These variations can be seen as an additional, so-to-speak ''dynamic'', matrix effect created upon projectile impact on the sample. For example, experiments and preliminary MD simulations of 20 keV C_{60} bombardment of ice samples indicate that the projectile creates a large number of protons in the excited surface region [18,56,57]. In the case of PS molecular samples, recent simulations also show that tens of C–H bonds are broken by 10 keV C_{60} projectiles around their impact point (a 25 Å diameter sphere) [54]. The excited nanovolume may therefore appear as a melting pot of interacting ions, radicals and molecules (i.e. the alchemist's mixture). The large sputtering yields also suggest the development of a plume of ejected species above the projectile impact point [58], a situation that reminds more the case of MALDI and, possibly, ME-SIMS than the supposedly ''clean'' processes induced by monoatomic ions, involving separate collision cascades and few sputtered species per impact. Because of the significantly different physics (and chemistry) at play, the correct interpretation of cluster SIMS spectra will require a thorough investigation of the involved processes. On the other hand, recent studies demonstrate that some of the aforementioned sample preparation procedures, e.g. metallization and matrix electrospray, have actually become quite versatile and robust, as witnessed by their successful application for high-resolution SIMS imaging [23,24,34,37].

Perhaps the solution of the dilemma (sample preparation procedures versus polyatomic bombardment) does not lie in the critical comparison but in the synthesis of the two approaches. This combined method is still in its infancy, but promising results have been/are being obtained. For matrix-diluted samples of Chain B of insulin (Fig. 1 and Ref. [10]) show that SF_5^+ projectiles provide an additional yield increase of a factor 4–15, depending on the ion polarity. The analysis of other peptides confirms the additional enhancement provided by SF_5^+ over Xe^+ in ME-SIMS [10]. For C_{60}^+ bombardment of Irganox 1010^{TM} molecules, gold metallization induces a complementary yield enhancement factor of 2 for the molecular ion and 8 for characteristic fragment ions [59]. The combination of Au_3^+ projectiles and silver metallization is also under test for the imaging of biological tissues [49]. Systematic investigations of those effects do not exist yet, but the mentioned observations and the virtually unlimited projectile/sample preparation procedure combinations justify some optimism.

7. Conclusion

Three sample preparation procedures used for molecular ion yield enhancement in SIMS, relevant to the concept of matrix-enhanced SIMS, have been critically reviewed. All these methods give excellent results under certain conditions. They appear to be, at times, interchangeable and, at other times, complementary. Some criteria of choice between these procedures are the type of application (e.g. structural analysis, chemical imaging), the nature of the analyzed sample (e.g. analyte in solution, real-world sample), the degree of knowledge of the system (e.g. complex mixture, unknown sample) and the equipment available in the laboratory. Even though the use of polyatomic projectiles seems, at first sight, more convenient, robust and versatile, one must recognize that they are submitted to similar constraints. Ultimately, the reviewed results suggest that combining polyatomic projectile bombardment with matrix-enhanced SIMS sample preparation procedures might be the best approach for molecular yield improvement in organic SIMS and high-resolution SIMS imaging.

Acknowledgements

The author thanks the Belgian Fonds National de la Recherche Scientifique (FNRS) for financial support. Barbara Garrison, Lekshmi Kailas, Ed. Smiley and Sami Yunus are gratefully acknowledged for proofreading the manuscript.

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