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A qualitative X-ray analysis of white and grey mineral trioxide aggregate using compositional imaging

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Mineral trioxide aggregate (MTA) is used in endodontics as a filling and sealant material. An earlier commercial formulation Grey MTA (GMTA) was liable to became progressively discoloured, and a whiter version (WMTA) has been introduced for cosmetic reasons. This study compares the composition and particle size distribution of the two formulations using energy dispersive X-ray analysis in a scanning electron microscope. Particle size is smaller in WMTA. X-ray analysis reveals similar major peaks (calcium, silicon and bismuth) but those of the minor elements aluminium, magnesium and particularly iron are considerably less in WMTA, which may account for the colour difference. Neither contains phosphorus, a major constituent of the original formulation.

Introduction

The use of X-ray signals derived from spectrometers for scanning electron images containing element-specific information was developed very early in the history of the electron probe microanalysis (EPMA) [1]. The practice of EPMA involves irradiating a specimen with a beam of electrons and subsequently collecting and analyzing the X-rays that are emitted. The detected X-rays are displayed in the form of spectrum displaying the x-ray count versus energy. Each element produces its own characteristic set of X-ray lines occurring at precisely defined energies. Measurement of these line energies provides a means of element identification [2, 3]. Images showing the distribution of specific elements can be obtained by using the X-ray signal to modulate the intensity of pixels during image acquisition. This can produce valuable qualitative information regarding the distribution of mineral phases and general microstructure [4]. In addition, scanning electron micrographs collected using the backscattered electron signal can provide complimentary information on compositional heterogeneity through the mechanism of atomic number contrast.

Mineral trioxide aggregate (MTA) was introduced to endodontics for treatment of the lateral root perforation and also as an ideal root-end filling material in surgical procedures [5–6]. Because of the potential discoloration effect of grey MTA, new "tooth colored" formula of MTA has recently been introduced to the profession for the same purposes [7]. Although many researches have been carried out on the clinical and biological characteristics of MTA during recent years, not much has been done on its chemical composition. The chemical composition and properties of MTA have been investigated by using energy dispersive spectrometer (EDS), X-ray diffraction analysis, fluorescence spec-

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trometer Rx and inductively coupled plasma emission spectrometry [8–11]. Elemental maps provide useful information for the analysis of various biological materials. It seems that the elemental mapping reveals the composition of structural phases of materials. However, no published study of MTA cements has been made using this technique. The purpose of this study was to evaluate and compare the distribution of the elements contained in WMTA and GMTA by using a combination of backscattered electron imaging and digital compositional mapping. This enables us to observe the basic morphology and to compare the elemental distribution.

Materials and methods

GMTA and WMTA [ProRoot MTA (Original) and ProRoot MTA (New tooth colored formula), Dentsply Tulsa Dental, Tulsa, Oklahama USA] were used. Samples were mounted in individual, pre-prepared 25.4 mm diameter resin (Araldite 502 + Epon 812, ProSciTech, Australia) discs to ensure compatibility with the electron probe micro analyser. Each disc contained a hole, drilled to a depth of 3 mm with 1 mm width. The cement samples were mixed with distilled water according to the manufacturers' instructions and were placed in the hole. The samples were then immersed in normal saline solution and allowed to set in an incubator at 37 °C for 48 h.

After setting, all samples were polished using 1 μm diamond paste, followed by carbon coating using a Dynavac CS300 (Dynavac, Australia) coating unit. A JEOL JSM6400 (JEOL, Japan) scanning electron microscope (SEM), equipped with a EDXA system (Oxford Instruments, Cambridge, UK) using "ISIS" software was used to perform the digital compositional mapping.

SEM operating conditions used were: 15 kV accelerating voltage, 39 mm working distance and 1 nA probe current. Energy dispersive X-ray spectra as well as secondary (SE) and backscattered electron (BSE) images were collected from each MTA sample at 600X magnification. The digital X-ray images were collected at 256 $\times$ 200 pixels.

Results

Optical examination of both WMTA and GMTA samples revealed the presence of coarse and irregularly shaped crystalline particles scattered throughout a

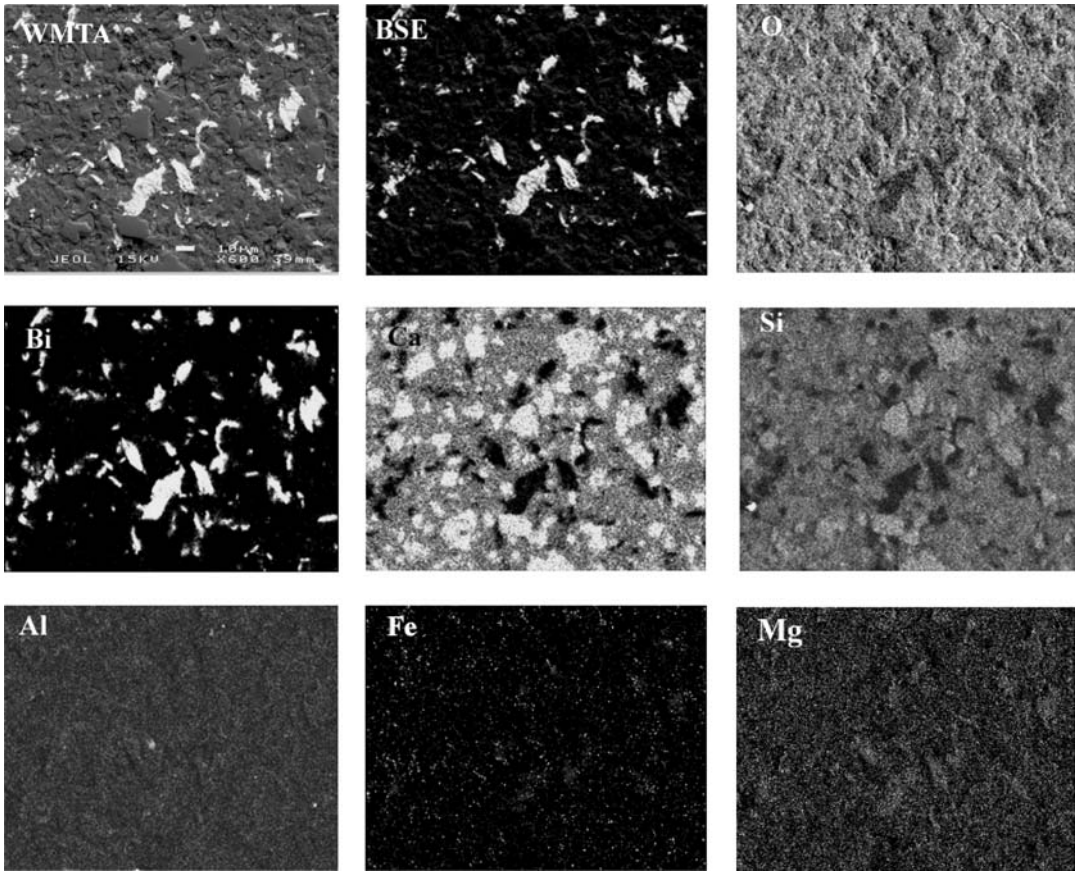

Figure 1 Scanning electron micrograph of WMTA (600×, Bar 10 μm) and compositional imaging of it: (BSE) backscattered electron photomicrograph and digital compositional images of the elements: (O) oxygen (Bi) bismuth, (Ca) calcium, (Si) silicon, (Al) aluminum, (Fe) iron and (Mg) magnesium. Note the similar X-ray pattern of distribution of calcium and silicon particles.

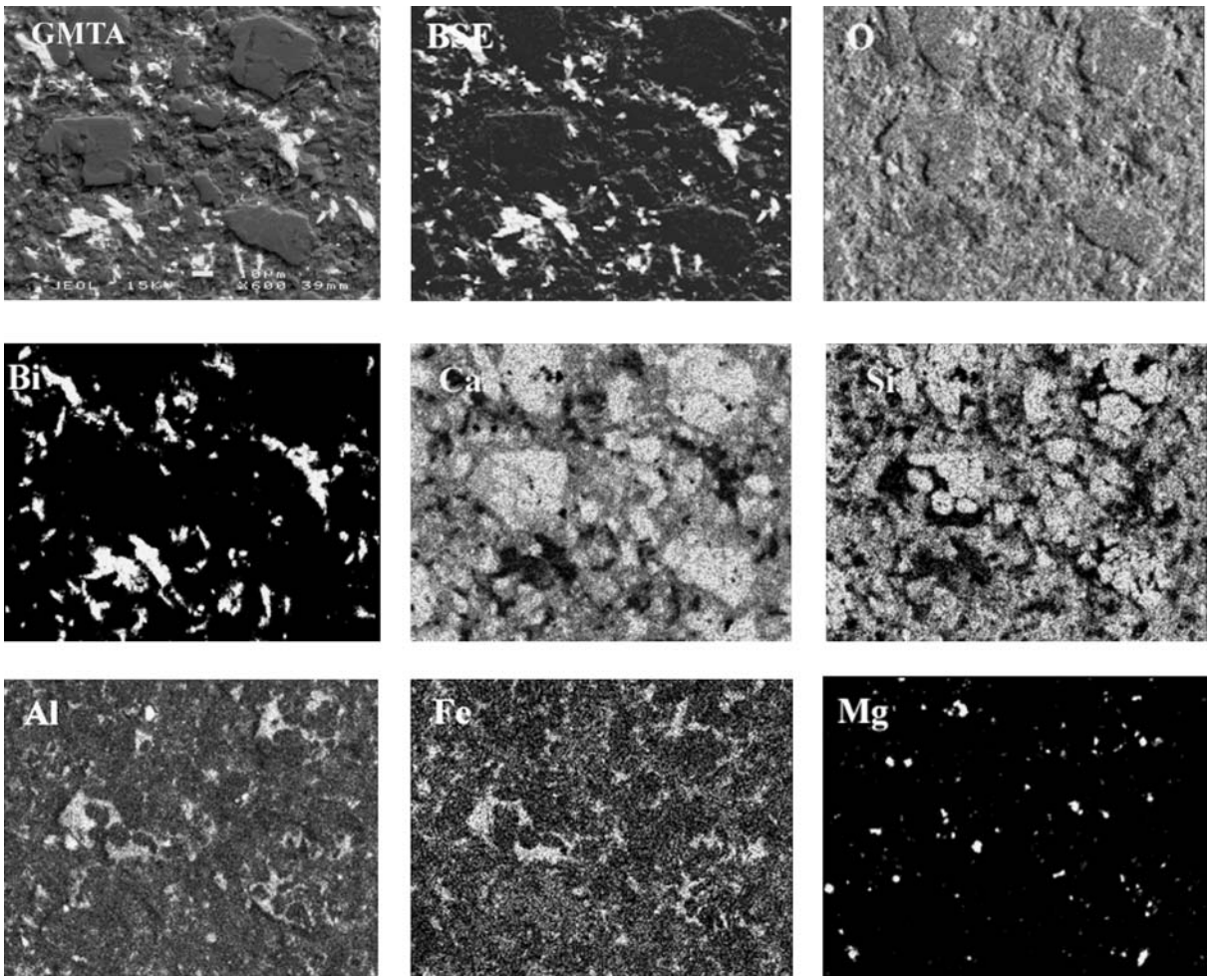

Figure 2 Scanning electron micrograph and compositional imaging of GMTA (600×, Bar 10 μm): (BSE) backscattered electron photomicrograph and digital compositional images of elements: (O) oxygen, (Bi) bismuth, (Ca) calcium, (Si) silicon, (Al) aluminum, (Fe) iron and (Mg) magnesium. Note the very similar X-ray pattern of distribution of aluminum and iron particles.

general groundmass of finer amorphous material. Careful inspection of Figs 1 and 2 clearly indicates that the overall size distribution of crystals observed in GMTA is significantly bigger (range, 5–50 μm) than that observed in WMTA (5–25 μm).

In both WMTA and GMTA, classes of particles were observed which appeared very bright in the SEM, indicative of a higher mean atomic number than the crystalline and amorphous phases. X-ray images of bismuth are given in Bi part of Figs 1 and 2 and demonstrate complete overlapping with these bright particles.

As is shown in Fig. 3, the peak intensities of major elements (calcium, silicon and bismuth) are very similar in WMTA and GMTA, but the peak intensities of minor elements (iron, aluminum and magnesium) are different. The iron peak intensities in WMTA are absent and aluminum and magnesium peaks are significantly less than that observed in GMTA.

Fig. 1 shows digital compositional maps of WMTA, showing the distribution of major elements (calcium, silicon and bismuth). This reveals that the pattern of distribution of calcium and silicon is the same.

Digital compositional maps of GMTA (Fig. 2) demonstrate the distribution of major (calcium, silicon and bismuth) and minor (aluminum, iron and magnesium) elements. As is shown in Fig. 2 the distribution patterns of calcium and silicon colocalise in two major phases of GMTA. The same distribution pattern is observable for aluminum and iron. Particles of magnesium are dense and do not colocalise with the other elements.

Discussion

The human visual process is capable of rapidly assimilating the information presented in the form of images, and problems can often be solved merely by determining where in a microstructure a particular constituent is localized [4].

The results of this study indicate that the size distribution of crystals observed in GMTA is significantly larger

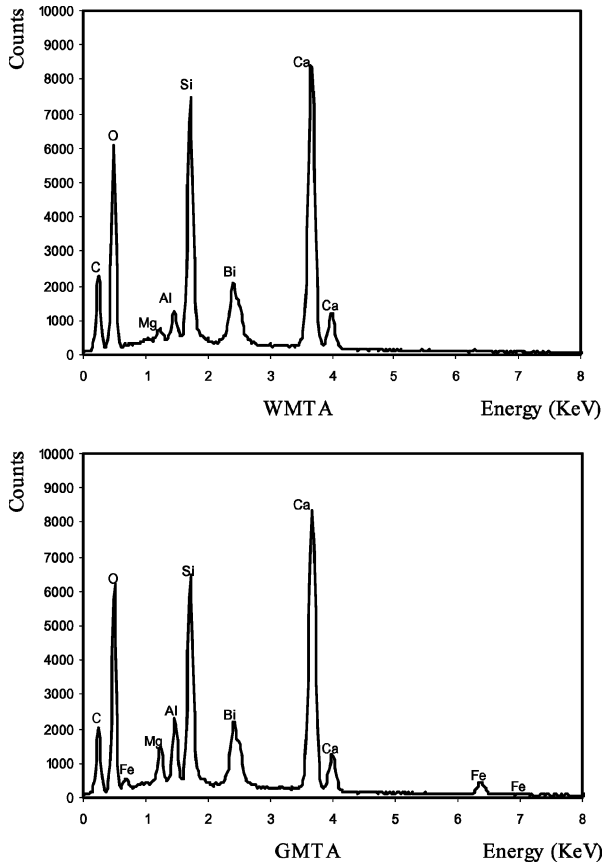

Figure 3 Energy dispersive X-ray spectrum of white and grey MTA. Note the iron peak intensities of iron are absent in WMTA, and the different height of Mg and Al peaks in the samples.

than that observed in WMTA (approximately 8 times). This finding reveals that WMTA provides a mixture with an overall finer texture. Portland cement (PC) has been compared with MTA in recent years; it was reported that MTA and PC appear to be almost identical chemically, macroscopically, microscopically and according to X-ray analysis except in the case of bismuth [9–12]. On the other hand, it has been shown that crystal size can affect the physical properties of Portland cements; smaller particle sizes increase the surface available for hydration and causes greater early strength [13]. Observation of smaller size distribution of crystals in the WMTA in this study suggests that its setting time might be less than that of GMTA and application of WMTA may be more appropriate in treatment procedures. As there is no publicized report on these issues, further research in this area is recommended. Spangberg et al. showed that when the smoother surface of the dental materials placed in direct contact with living tissues, less irritation is caused [14]. Therefore, the use of WMTA with small size particles and finer texture is more advantageous in endodontic treatments in comparison to GMTA.

The major research on chemical properties of MTA has been done by Torabinejad et al. [8] and in several other articles the compositional structure of MTA is compared to Portland cement [9–12]. The results given in Torabinejad's article do not indicate the actual amount of elements, as the amounts are reported in the two amorphous and crystalline phases separately. Furthermore, as the proportion of phases is unknown, the data do not refer to the proportion of elements in the whole cement. Another point of interest is that it was reported that calcium and phosphorous were the main components of MTA [8]. The results of this study however, showed that the major elements in both types of MTA were calcium, silicon and bismuth respectively. These results appear to be entirely consistent with information supplied by the Dentsply Tulsa dental company, who do not report phosphorus as a significant element in MTA [15]. Therefore, it appears that a significant change in composition has occurred since this material was first proposed as a root-end filling material by Torinbinjad et al. in 1993.

Both MTA specimens clearly show the presence of the intentionally added bismuth oxide, which can be seen as areas of higher intensity (Figs 1 and 2). These particles entrapped in the amorphous phase of both types of the MTA provide radio opacity for clinical tracing purposes.

As is shown in Figs 1 and 2 oxygen is distributed throughout the crystalline and amorphous phases of white and grey MTA. This reveals that all the elements are present in their oxide form. The X-ray intensity maps of the minor elements aluminum, iron and magnesium, shown in Figs 1 and 2 indicate that their distribution is significantly different when comparing WMTA to GMTA. In each case the X-ray intensity maps reveal an even distribution of these elements (Mg, Al, Fe) in WMTA while they form dense and localized regions in GMTA (c.f. Figs 1 and 2). The most significant difference can be found in the observed distribution of iron which seems to be essentially absent for WMTA. This difference is also clearly observed in the relative peak intensities for iron (Fe) in the X-ray spectra obtained from WMTA and GMTA as shown in Fig. 3.

Previous work [16] indicated oxides of most of the elements found in either WMTA or GMTA such as MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2 and Bi_2O_3 tend to be colourless, white or perhaps a pale yellow, whereas oxides of iron are dark, FeO being black. It therefore seems reasonable to suspect that the absence of significant FeO or Fe_2O_3 in WMTA is the dominant factor in the change in colour from grey to white when comparing GMTA and WMTA.

Conclusion

This study reveals that WMTA provides a mixture with an overall finer texture in comparison to GMTA. Differences in the iron concentration as observed in the X-ray images may account for the WMTA color difference when comparing to GMTA.

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