

## DETECTION OF LIGHT ELEMENTS IN SEDIMENTS BY X-RAY MICROANALYSIS (SEM/EDS).

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Interest in calcium carbonate formation and dissolution in the ocean has increased due to the central role of these reactions in the ocean's response to the increasing partial pressure of carbon dioxide (pCO<sub>2</sub>) in the atmosphere, and also to the sequestration of carbon dioxide in subsurface carbonate reservoirs and saline waters [1]. Components of the carbonate system in sediments traditionally have been characterized by simple gravimetric determination of calcium carbonate. SEM-based X-ray spectrometry has been used to determine elemental concentration and distribution in mineralogical, geological and material research in microscale [2, 3]. However, X-ray production from carbon tape and carbon coat, as well as from the aluminium sample holder itself, prevent an accurate detection of carbon and aluminum in EDS mainly in small specimens [4]. This study proposes a new approach to detect carbon by SEM/EDS using sediments of the Jaguaribe River estuary as a test sample.

The SEM/EDS strategy involves sample mounting disk and glue. Mounting disk: Fragments (10 x 10 x 0.5 mm) of gold target [BALTEC (B 8010 072 21)] were adhered on aluminum stubs with silver paint (Sigma) and used as sample mounting disk. Controls: (i) Mounting disk were covered with a thin film of adhesive cyanide acrylate ester (Loctite Super\_Bonder<sup>®</sup>), (ii) granulated calcium carbonate (MERCK) were adhered on mounting disk with a thin film of adhesive cyanide acrylate ester, (iii) granulated calcium carbonate (MERCK) were deposited on mounting disk without adhesive. For counterproof, granulated calcium carbonate (MERCK) was adhered on carbon double face adhesive tape. Sediment: Estuarine sediment were collected 4-25°45" S; 37-46°11" W at 3 to 8, 23 to 28, 43 to 48, 73 to 78, 83 to 88 cm depths in the core. These depths were selected based on their carbonate content [5] and representing the lowest and highest carbonate concentrations. Lyophilized samples (100 mg) were adhered on gold mounting disk with a thin film of adhesive cyanide acrylate ester. Alternatively, samples were set on mounting disk without glue and kept 24 h at 50 °C before analyses. In all cases, glue was dried at room temperature. Morphological and analytical data were obtained with a SEM EVO 40 XVP ZEISS operating at 25kv and coupled to an energy dispersive spectrometer IXRF with ZAF correction. Samples were maintained at -20 C with a Deβen coolstage during SEM/EDS analysis.

Carbon was not detected by SEM/EDS in gold mounting disk covered with a thin film of adhesive cyanide acrylate ester. The calcium carbonate powder (MERCK) occurs as irregular aggregates. Carbon, oxygen, calcium and gold were identified in the X-ray spectra. An overlap of carbon, oxygen and calcium is noteworthy in EDS distribution map (Fig. 1). Carbon was not detected in gaps among calcium carbonate aggregates. Image damage occurred when sample was disposed on gold mounting disk without glue probably due to the heating caused by electron beam. In the counterproof, the morphology of calcium carbonate was the same. However, carbon signal was indistinguishable between double face adhesive tape and calcium carbonate grains by microanalysis.

Aggregates of the particulate material process was revealed by morphology of the estuarine sediments. Sediment grains were aggregates with considerable size and morphology diversity. Al and Si were the predominant elements in aggregates. However, C, O and Ca were detected in several aggregates. In EDS distribution map, the overlapping of C, O and Ca strongly suggest calcium carbonate within sediment aggregates (Fig. 2).

The new procedure proposed was efficient to identify calcium carbonate in estuarine sediment aggregates. Carbon signal from adhesive cyanide acrylate ester (Loctite Super\_Bonder<sup>®</sup>) was not detectable by SEM/EDS. The choice of gold was due to its uncommon occurrence in the environment. Moreover, conductive mounting disk and controlled temperature were critical to avoid sample damage during analysis.

Acknowledgment:

CNPq INCTI TMCOcean 573601/2008-9

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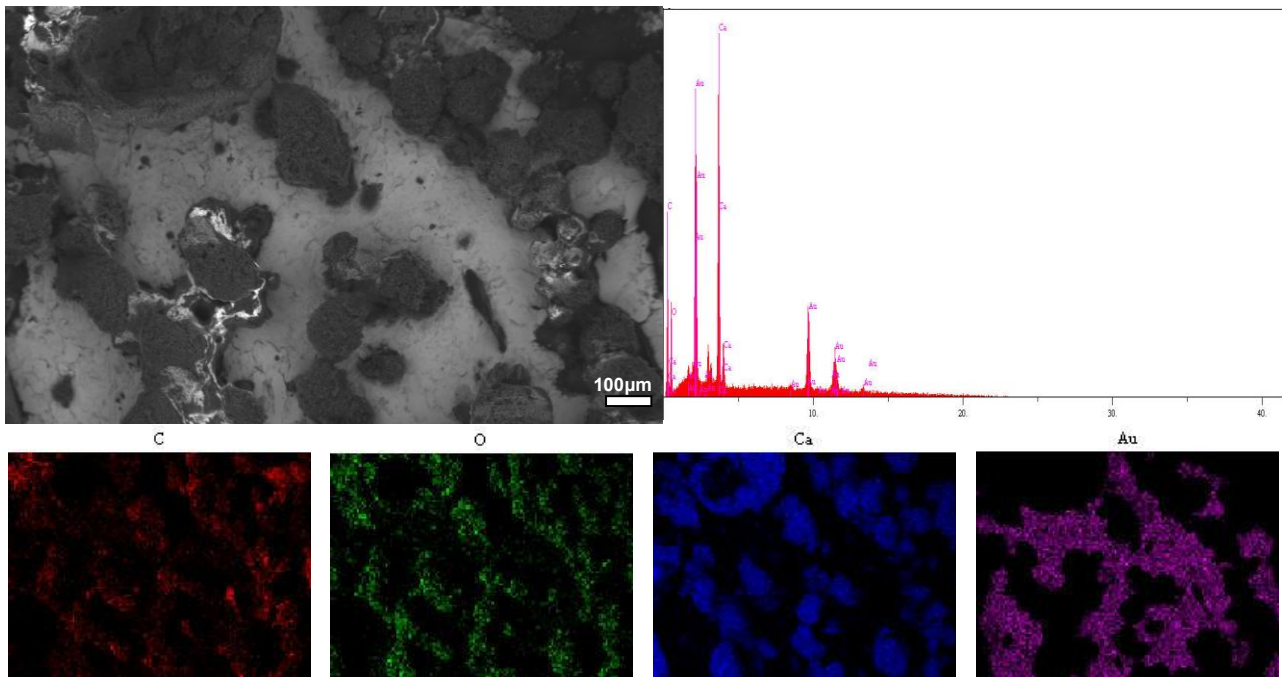


Figure 1 - Aggregates of calcium carbonate adhered on gold stub with *Loctite Super Bonder*<sup>®</sup> glue. EDS spectrum showing only C, O, Ca and Au. Carbon from epoxy glue film was not detectable in distribution map.

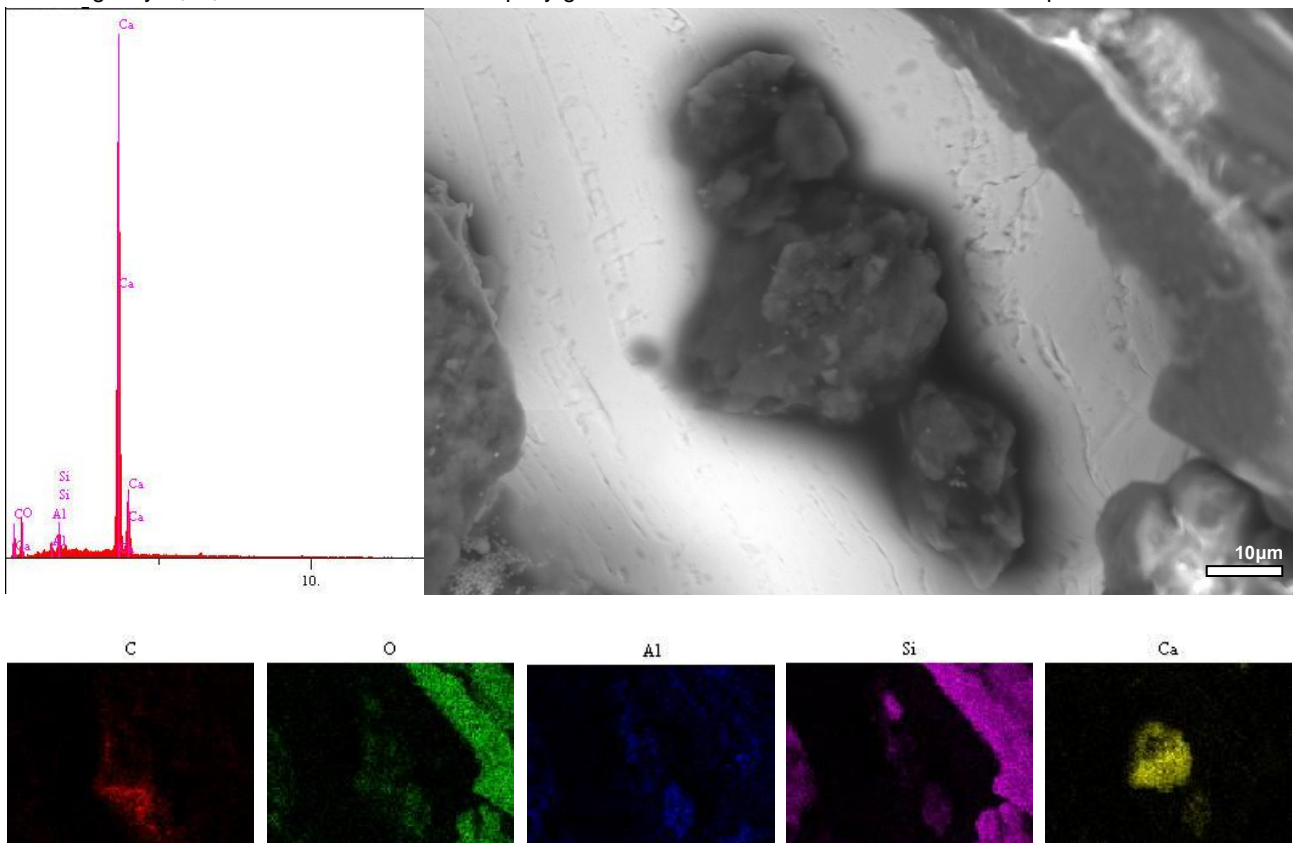


Figure 2 - Jaguaribe River sediments from 23-28cm deep fraction adhered on gold stub with *Loctite Super Bonder*<sup>®</sup> glue. Sediment aggregates showing diversified morphology and size. Punctual EDS spectrum (+) detecting C, O, Al, Si and Ca. Note overlapping of C, O and Ca in distribution maps.