

High-throughput MeV ion beam analysis – quantitative full stoichiometry imaging of a granite

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ABSTRACT

MeV Ion-Beam analysis (IBA) can quantify the whole periodic table, provide tomographic information, analyse elements up to 100 μm depth, and achieve down to nm depth resolution under ideal conditions. This brings along a high degree of instrument and data analysis complexity. Only recently, optimised instrument geometry and precision on the hardware-side and artificial intelligence, modern computing power, and new nuclear cross-sections on the software-side enabled analysing the IBA spectra effectively and with only little human interaction. The increased throughput reinvents IBA as an elemental imaging technology.

This work presents a $5\times 5\text{mm}^2$ imaging of a granite sample with 100×100 pixels using four IBA methods measured and analysed within 24 h. This demonstrates the capabilities of the newly developed software and hardware solutions. The analysis reveals SiO_2 , an Al, and a Fe rich phases in the granite. The present elements and their concentrations match typical granite phases.

1. Introduction

Materials are a key component in any technological development and product, making material development and characterisation a key technology for many material inventions [1]. Analysis methods enable a quantitative picture of processes inside and the composition and purity of materials. Ion-Beam-Analysis (IBA) probes materials using scattering of MeV ions, typically H and He, with the sample atoms. IBA offers unique analytical possibilities through its sensitivity for the whole periodic table, including light elements such as lithium and hydrogen and its superior detection limits compared to electron or x-ray based local analysis methods [2]. The origin lies in the physics of bremsstrahlung and energy-loss differing strongly between ions, electrons, and photons and the MeV energy enabling access to nuclear information. IBA comprises several sub-methods each exploiting certain interaction products and physics. Among these sub-methods, Rutherford-Backscattering Spectrometry (RBS), Particle-Induced X-ray Emission analysis (PIXE), Nuclear-Reaction-Analysis (NRA), and Particle-Induced Gamma-ray Emission analysis (PIGE) represent a particularly powerful subset [3]. Fig. 1 presents the potential contributions of each sub-method to a stoichiometric IBA analysis, demonstrating an access to the whole periodic table by combining the four methods in a single measurement.

Analytical setups combine these four sub-methods for extending

their analytical power [4]. State-of-the-art setups enable absolute quantification with statistical uncertainties down to $\sim 1\%$ [5,6] and Limits-of-Detection (LoD) in the ppm range in many cases. The absolute uncertainty is usually limited by the required measured input data, in particular the stopping power and the reaction cross-sections. IBA is typically conducted in the form of a point analysis where a single point or a small set of points on selected locations on a sample are analysed. Mapping analysis adds lateral (2D) or even tomographic (3D) information requiring significantly more points and therefore measurement time. Typical IBA acquisition times of several minutes to hours per point and manual data evaluation prevent acquiring a point quantity suitable for producing images. Due to the easier interpretation, mapping is mostly related to PIXE, so-called μ -PIXE, missing out the light elements such as Boron or Lithium and the tomographic information. As demonstrated in Fig. 1, it is advantageous to include more IBA methods in the mapping analysis to access the whole periodic table. Numerous other methods enable access to the whole periodic table, some with even better detection limits, but the resulting combined information can suffer from inconsistencies. With IBA, even when combining several detectors, projectile species (H, He...), and projectile energies, the measurement is consistent by using the same detectors, physics, analysis location, input data, and a consistent data interpretation.

IBA mappings with resolutions in the order of 256×256 pixel [7,8]

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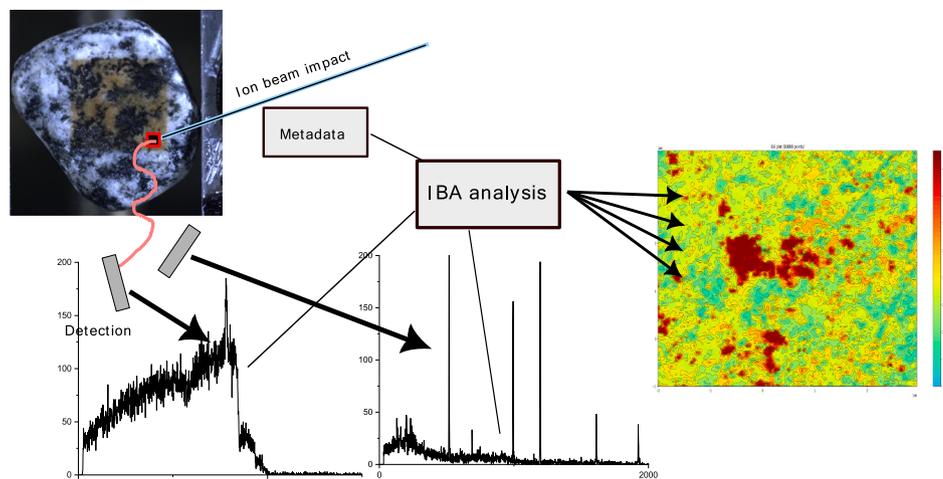


Fig. 2. Workflow of IBA. The pixels are obtained by moving the sample to a matrix of discrete positions. Each detector generates a spectrum (actual measured spectra are shown) for every pixel on the sample. These spectra, together with the metadata, are fed into the analysis software. The accumulated evaluations are combined to elemental sample maps.

every pixel. This approach avoids image plane distortions, since the sensors attached to the piezo motors provide the lateral coordinate.

Three software modules acquire, process, and display the IBA results. The PIXE data is processed using GUPIX3.03 [23], the PIGE, NRA, and RBS data using SimNRA 7.03 [10]. The AutoNRA software [13] operates these programs in a parallelized processing for batch interpretation of the 40,000 spectra plus 10,000 metadata files and adds additional fitting algorithms to SimNRA to find global and local minima more efficiently. The processing runs on a 64-core workstation PC with up to 1500 iterations per spectrum, requiring about the same 24 h as the data acquisition. AutoNRA requires the user to enter a reference composition of the approximate sample composition, which is derived from the peaks found in the IBA methods and a first manual SimNRA interpretation of a single data point. SimNRA is set to use the standard settings plus “multiple scattering” and electronic stopping power data using SRIM2013. Gupix is fitting using the “iterated matrix solution” with O as invisible element. The software loads all resulting elemental depth profiles and generates the plots presented below using a linear interpolation algorithm.

The sample is collected from regular gravel. After wiping with propanol, it is installed into the end station. Further sample preparation is not required, although this preparation represents drawbacks in terms of not removing weathering artefacts and not providing the ideal analysis geometry. The sample surface is not perfectly flat but its normal is oriented towards the incident beam by clamping it onto the backside of a slit holder made from aluminium. The samples irregular non-polished surface introduces additional uncertainties into the spectral evaluation. For the thick and in-depth homogeneous sample, the effect is small and relates to geometric differences in the particle energy loss for the varying impact angles of the projectiles. In the given case, SimNRA and Gupix analyses comparing impact angles from 0 to 20° reveal additional uncertainties of 3 % (RBS, NRA, PIGE) and 0.7 % (PIXE), respectively, introduced by the non-polished surface. Within 24 h of continuous measurement, a 5x5 mm² mapping with ~ 9 s = 70 nC per point is acquired. This corresponds to a map of 100x100 pixel with 50 μm analysis spots. The spectra contain about 20,000 counts for RBS, NRA, and PIGE and 500,000 counts for PIXE. The related total uncertainty in the elemental concentrations is 10 %. The raw data is published separately [24].

After IBA, the sample is checked for nuclear activation using a Berthold LB124 scintillation detector. No activity beyond the natural level is detected, allowing for handling of the analysed sample in regular laboratories. Most of the potential products from (p, n) reactions of the detected elements are short lived with half-lives of minutes or less. These radioactive isotopes, if produced at all, will decay before the operator

takes out the sample, hence cannot be detected. MeV protons can result in a few long-lived activation products such as Ca-41 (from K) or Co-56 (from Fe), but the reaction cross-sections are small at 3 MeV, not resulting in an activity above the detector LoD and the German free handling limit according to calculations similar to [25].

3. Results

Fig. 3 1) shows a photography of the sample after analysis. The sample is slightly affected by the ion impact, visible as a darkening of the white parts of the granite. This effect is often observed in (semi-) transparent materials and originates from lattice damage induced by the ion impact cascades. This structural damage cannot influence the IBA result, which relies only on the elemental composition.

The analysis yields signals above the LoD for 11 elements (C, O, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Sr), displayed in Fig. 3 a) to k), with the lowest concentration found for Sr and Mn on the 500 ppm level. A search for Li (LoD = 1 %), F (LoD = 1 %), and B (LoD = 10 %) yields no presence of these elements according to the related NRA (α-emission) and PIGE (γ-lines) reactions. Consequently, PIGE provides only negative information in this case, which is also important. The information on C and O are related to the RBS analysis, while the heavier elements are mostly provided by PIXE due to its advantageous statistics compared to RBS. RBS shows flat depth profiles within the given limits. With the given 70 nC ion fluence, the lowest LoD is 14.8 ppm for Ti. H and He cannot be detected using the presented analysis, but besides these elements, the presented maps can be assumed to represent the full stoichiometry.

The comparison of the optical and elemental images reveals three major phases, a black Fe, Mn, Ti-rich, a white Si-rich phase, which is not darkened by the ion beam, and another white Al-rich phase. In most locations, a thin surface layer of mostly carbon is found with a thickness of up to 2.0·10²² atoms/m² and a median of 0.87·10²² at./m² thickness (Fig. 3h), corresponding to ~ 250 nm and 76 nm, respectively, assuming pure graphite. In the bulk, the C content ranges between 0 and 2.4 at.% with a median of 1.2 at.%, see Fig. 3i). The Si-rich part incorporates a higher average concentration of C compared to other regions. The optical image indicates the carbon is not present as pure graphite layer, which would be a grey colour impression, but rather as a surface near enrichment not resolved within the given depth resolution.

Trace amounts of Sr of up to 0.05 wt (weight) % are present in the Al rich phase, but no Sr is found in the Si and Fe rich parts. This suggests the Al rich phase is a plagioclase feldspar ((Na,Ca)(Si,Al)₄O₈) where Sr substitutes Ca atoms. In the Fe rich parts up to 11.2 wt% of Fe is found. Together with the presence of Al and Si this suggests a Biotite (K(Mg,Fe,

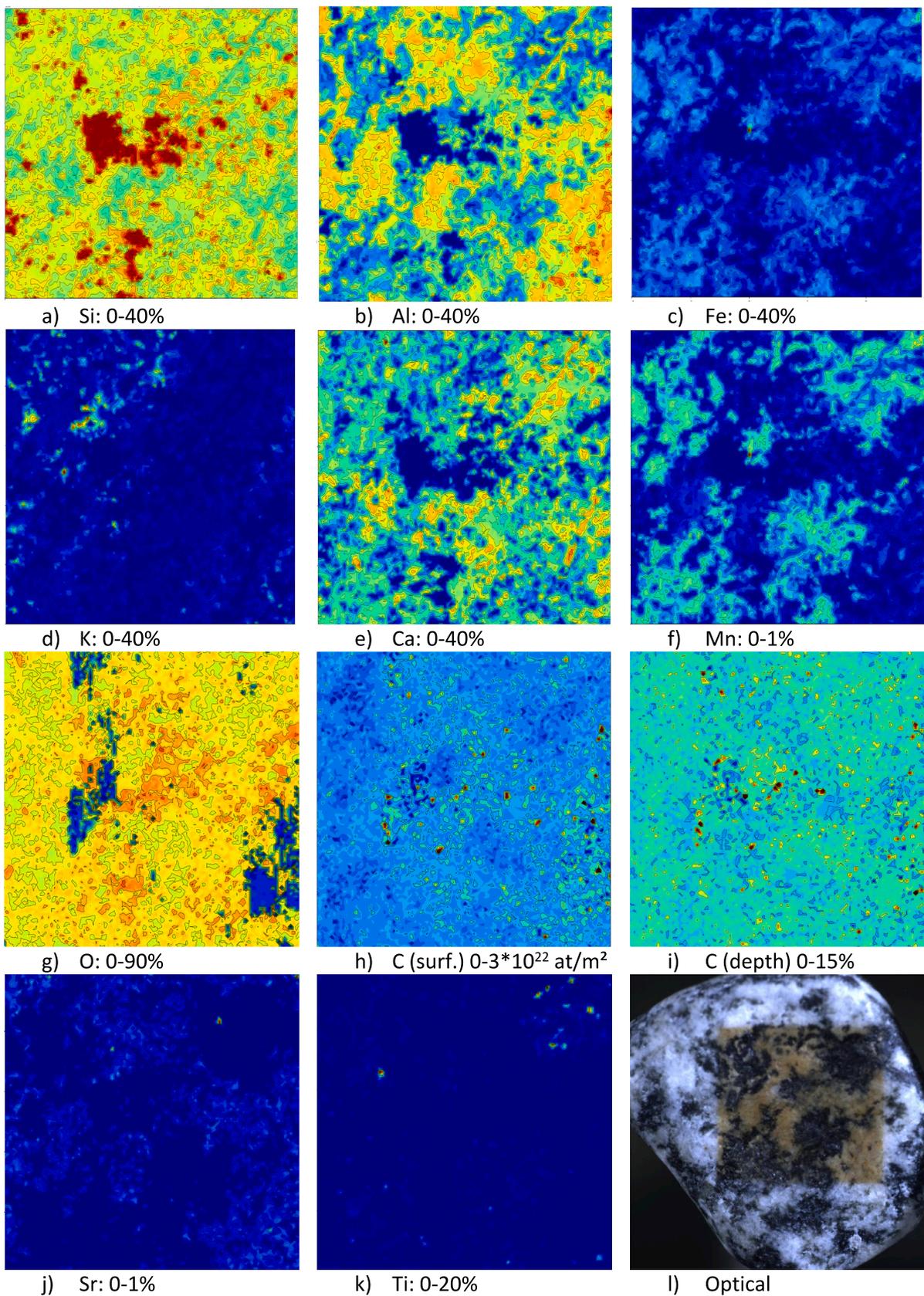


Fig. 3. Observation camera image (l) and 10.000 points elemental concentration mapping (a-k) results of the 5x5 mm² scan on the granite using IBA. The 5x5 mm² analysis region is clearly visible by a darkening of the white parts of the granite in the optical image. Black parts of the granite can be attributed to Fe, Mn, Ti rich and bright parts are either SiO₂ or Al rich compounds. Concentrations are on a linear scale of 0 (dark blue) to the given maximum percentage (dark red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Mn)₃(AlSi₃O₁₀)(OH)₂). The median over the whole area is at 3.4 wt%. Mn is highly correlated with Fe with up to 0.27 wt% Mn in the Fe rich parts and a median of 0.08 wt% over the whole area, supporting the Biotite assumption. Similarly to Mn, Ti is strongly correlated with Fe, but it is less evenly distributed. Most of the Ti is found in a few single data points reaching up to 13.5 wt% with a median over the whole surface area of only 0.08 wt%. This indicates minor inclusions of ilmenite (FeTiO₃). Ca is found in the Al and the Fe rich parts relatively evenly distributed with up to 20 wt% and a global median of 8.6 wt%. The Al rich phase contains up to 22.5 wt% Al with a global median of 11.6 wt%. The combination of Ca and Al weight percentages and the absence of Na clarifies the plagioclase feldspar as anorthite (CaAl₂Si₂O₈, with 19.4 wt% Al and 20 wt% Ca) dominated.

In the Si rich part, no Ca can be found. K reaches up to 8 wt% concentration with a median of 0.3 wt% and is a part of the Biotite mentioned above (Biotite nominal 8.4 wt% K content). Si reaches 46 wt% in the Si rich part, but is present in all phases with a median of 28.3 wt%. The weight percentage in the Si-rich phase fits perfectly to Quartz (SiO₂) with 46.7 wt% Si. Cl is uncorrelated to the other elements with a median concentration of 0.1 wt% and a maximum of 0.5 wt%.

Regarding the light elements, O is found mostly homogeneously distributed over the sample in concentrations of a median of 60.6 atomic % and a standard deviation of 2 atomic %. Parts of lower O concentrations (blue) are related to non-convergent fits. This problem typically affects < 1 % of the data points and can be excluded through a Z-score filtering. In the presumed SiO₂ rich part, higher concentrations of O = 65 % and Si = 32 % (=46 wt%) are found. This supports the assumption of pure SiO₂ regions with its nominal 33.3 % Si and 66.6 % O. Carbon is at a median concentration of 5.8 atomic % in the bulk, but statistical fluctuations due to limited counting statistics are significant for this element. In the SiO₂ regions, the C concentration is slightly below the average value.

4. Conclusions

The combined IBA using scattered ions, x-rays, and gamma rays provides a unique insight into the full material stoichiometry of the analysed sample. The presented IBA combines several smaller advances in software and hardware to a large advance of the technological level. The analysis identified 3 phases, SiO₂, a Fe-rich and an Al-rich phase. The composition and the detection limits are consistent with a full stoichiometric characterisation. Light elements such as Li, F, and B are not found.

The presented granite analysis demonstrates the strength of IBA elemental imaging. The sample features an intermediate complexity in terms of the number of elements (11 elements present in the sample) and the complexity of the elemental depth profiles (2 layers), which are found to be flat beyond a surface C layer. Yet the sample is a common sample type. The IBA is conducted without any preparatory steps or manual interaction, except for a basic cleaning, resulting in a high degree of automation. IBA reveals the potential resource value of the investigated granite and its local distribution showing potential extraction routes through the identification of the present phases.

Elemental compositions are highly important in many modern fields. In leaching of ores, the resulting leached sample and the missing elements would become visible on a grain/phase resolved scale, in contrast to a global view provided by dissolving methods. The elemental composition represents the state-of-charge of a battery cell, which it can locally measure without measuring a voltage. Processes in biology and pharmacology rely on the μm-resolved distribution of elements. Surface engineering requires minimal detection limits for coating development and quality control. Material development can be accelerated using the additional information revealed by IBA, accelerating finding solutions for climate change and the energy transition. Consequently, this work is the starting point for extending the use of IBA in industry, quality control, and research.

The technological advances of the last years yield major benefits in terms of accuracy, throughput, sample size, and versatility of IBA. Beyond state-of-the-art methods such as μ-PIXE, EDX or XRF it enables a full stoichiometric characterisation including trace quantities such as the detected Sr and light elements such as O, Li and B. The applied discrete mapping with fixed beam together with a full fitting of all spectra for each pixel represents a universal approach suitable for all lateral and sample scales, unifying former individual solutions for each length scale. The investigated scale is only a matter of the manipulator travel range, giving access to all spatial scales within a single device. This unification opens up a wide range of IBA applications in science and industry, similar to the widespread use of electron and x-ray microscopy. Further developments will allow for another 100-fold increase of the detector throughput via multi-detector setups and ASICs for RBS, NRA, and PIGE (PIXE SDDs already use ASICs), opening the path towards Megapixel tomographic IBA within this decade.

CRedit authorship contribution statement

S. Möller: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **K.F. Muzakka:** Software, Formal analysis. **D. Höschel:** Methodology. **M. Finsterbusch:** Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Soeren Moeller reports a relationship with Aachen Ion Beams UG that includes: board membership and equity or stocks. Daniel Hoeschen reports a relationship with Aachen Ion Beams UG that includes: board membership and equity or stocks. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data available at DOI 10.5281/zenodo.13944189

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