Three-dimensional phase separation and identification in granite

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**ABSTRACT**

Typical granite is mainly composed of quartz, plagioclase, and alkali feldspars, together with some smaller fractions of ferromagnesian phases and trace phases. The occurrence and abundance of these minerals can be determined by destructive methods, but the three-dimensional (3D) visualization of these mineral structures is very difficult. For geological samples, X-ray microcomputed tomography (μCT) is a very powerful tool to visualize 3D structures. However, μCT imaging is based on the X-ray linear attenuation coefficient, which depends on atomic composition, density, and X-ray energy, sometimes making it hard to identify different phases inside the sample. This problem can be overcome by combining μCT with other techniques that provide chemical information. The combination of μCT with micro-X-ray fluorescence (μXRF) and X-ray diffraction (XRD) allows segmentation and identification of the different minerals at the surface of the sample. Combining this information with the 3D density model obtained through μCT scanning of the granite allows 3D phase identification.

In this paper the results of the analysis of a representative Precambrian granite by these three complementary techniques are discussed and combined with the results of more traditional techniques like thin-section petrography. Although the granite sample is shown to be very heterogeneous, correct phase identification in 3D is obtained.

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**INTRODUCTION**

For several years now, X-ray microcomputed tomography (μCT) has been widely used to visualize and analyze geological samples in three dimensions (3D) (Ketcham and Carlson, 2001; Van Geet et al., 2001; Ikeda et al., 2004; McCoy et al., 2006; Zabler et al., 2008; Cnudde et al., 2009a, 2009b) and has found many other applications in areas such as paleontology, medicine, and biosciences (Dierick et al., 2007; Bauer and Link, 2009; Van den Bulcke et al., 2009). The great advantages of μCT are its nondestructive nature and its potential to separate the different phases in 3D present in a sample. For example, in sandstone with pyrite fragments, three phases can clearly be discriminated: air (or pores), sandstone grains (SiO2), and pyrite (FeS2) (Dewanckele et al., 2009). Since all phases have very different atomic composition and density, phase identification is straightforward due to the large difference in the X-ray linear attenuation coefficient of the three components. Unfortunately this is not the case for more complex rock types such as igneous rocks composed of phases with very similar attenuation coefficients (Gualda and Rivers, 2006; Jerram and Higgins, 2007). Segmentation can be improved by taking high-resolution and high-quality scans, but some minerals, like plagioclase and quartz for example, remain hard to separate due to their complex mineral structures and similar attenuation coefficients.

Another drawback is that chemical information is not readily available from laboratory-based CT data because attenuation depends both on atomic composition and density of the sample components as well as on the applied X-ray energy. One possibility to overcome this problem is the use of dual energy scanning. By scanning the same sample at two different tube voltage settings, the effective atomic number $Z_{eff}$ and the real density can be retrieved, as demonstrated for carbonate reservoir rocks (Remeysen, 2007; Remeysen and Swennen, 2008) and sandstone samples (Long et al., 2009). Another solution is offered by the combination of μCT with other techniques. De Samber et al. (2008a, 2008b) combined synchrotron-based X-ray fluorescence (XRF) tomography with laboratory-based μCT to study in 3D the accumulation of metals within specific organs of the water flea Daphnia magna. Pereira et al. (2007, 2009) performed similar research on breast tissue samples. The internal structure of bones was investigated with the combination of these two techniques by Lima et al. (2008a, 2008b). Cnudde et al. (2009c) combined laboratory μCT with several synchrotron-based and traditional methods for a complete characterization of a sandstone core. A similar approach was used by Baraka-Lokmane et al. (2009) to characterize sandstone cores. To minimize the misalignment problems associated with two separate measurements, Sasov et al. (2008) presented a compact μCT/μXRF scanner for nondestructive 3D chemical analysis of small samples. This instrument uses a photon counting CCD (charge-coupled device) to detect fluorescent radiation, which is reconstructed using an iterative algorithm to take the self-absorption into account.

In this paper, a combination of 3D μCT and 2D μXRF mapping is proposed to provide three-dimensional chemical information in a nondestructive way. This methodology is applied to an igneous rock sample, in which different minerals are discriminated and identified based on these two techniques. The results are compared to other destructive techniques such as XRD and thin section microscopy. It must be noted that the sample used serves as a proof of principle for the combined use of both techniques, and although this particular sample is not valuable, the nondestructive nature of the technique should be stressed.

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MATERIALS AND METHODS

For this research, a sample of Yellow Rock type granite was prepared. A small cylindrical sample with a diameter of 9.57 mm and a height of 8 mm was used for the combined analysis with μCT and μXRF. The sample had one polished and one unpolished flat surface (Fig. 1), although some damage can be observed at the edges.

The Precambrian Yellow Rock is a granite originating from China and is often used as a natural building stone for floor, wall, or decorative purposes. The denomination Yellow Rock is only one of the commercial names: synonyms for the yellow to reddish colored granite are Giallo Padang, Giallo Yellow, Dawa Yellow, Rustic Yellow, Desert Gold, etc. The international code or name for the granite is G682. Most applications of granite as a building material are based on its good technical properties. All granites are characterized by low porosity, high compressive strength, and low water absorption. The decorative purposes of the Yellow Rock granite are based on its large colorful minerals and its light glitter of different colors obtained after polishing. Therefore Yellow Rock granite is ideally suited for structural, chemical, and mineralogical characterization as some of the mineral phases can already be distinguished with the naked eye.

μCT scanning was performed at the Ghent University Center for X-ray Tomography (UGCT—http://www.ugct.ugent.be) (Masschaele et al., 2007). The flexible setup of the μCT scanner (Fig. 2) allows us to use an optimal configuration for each sample, resulting in very high-quality CT images. Two different X-ray tube heads are available, one with a thin transmission target for high-resolution scanning, and one with a directional target for larger samples that need more X-ray flux and have less stringent demands on the system resolution. All images were acquired by the Varian PaxScan 2520V a-Si flat-panel detector with CsI scintillator. This detector has a surface of 1496 by 1880 pixels of 127 × 127 μm².

In this study, the transmission target was used for the small sample, and the X-ray source was operated at a tube voltage of 80 kV and a target current of 100 μA, resulting in an effective target power of 8 W. With source-to-object distance of 47 mm and source-to-detector distance of 820 mm, a voxel volume of 7.273 μm³ could be obtained. The required detail detectability is easily achieved by the transmission tube head. The beam hardening filter used consisted of 500 μm copper and 200 μm aluminum. The total scan time for 1000 projections of eight frames with an exposure time of 1 s was ~3 h.

To avoid disturbing cone beam effects at the top and bottom parts of the sample (Turbell, 2001; Vlassenbroeck, 2009), the cylindrical sample was positioned with its symmetry axis perpendicular to the rotation axis.

All tomographic data sets were reconstructed using the software package Octopus (http://www.xraylab.com; Vlassenbroeck et al., 2007), which allows us to perform dual threshold segmentation, segmentation cleaning, object separation, and object labeling based on equivalent diameter or maximum opening. The 3D renderings were made in the commercial software package VGStudioMax.

An Eagle III (built by EDAX) μXRF laboratory instrument was used to obtain 2D elemental distributions at the surface of the granite. This instrument is equipped with a 40 kV
Rh X-ray tube with a glass polycapillary as the focusing element. The XRF intensities are collected with a liquid-nitrogen-cooled Si(Li) energy dispersive detector. The \(\mu\)XRF measurements were performed in vacuum using a \(\mu\)-beam with a focal spot size of \(\sim225\ \mu\m\) full width at half maximum. The mappings consist of 51 by 51 pixels with a pixel size of \(200 \times 200\ \mu\m^2\). Raw XRF spectra were analyzed and converted into net peak intensities by the nonlinear least-squares fitting program AXIL, which is dedicated to handling typical problems associated with XRF analysis such as background determination, peak overlap, escape peaks, and other spectral artifacts (Vekemans et al., 1994). This laboratory technique has some advantages over SEM-EDX imaging, such as the possibility to scan larger samples, the lower background signal, and no sample preparation (Newbury and Davis, 2009). To improve the interpretation of the elemental distributions, similar regions in the mapping were grouped using a K-means clustering algorithm (Vekemans et al., 1997).

X-ray diffraction (XRD) patterns of the Yellow Rock granite sample were collected on a Philips X’PERT system with a PW 3710 based diffractometer, equipped with a Cu tube anode, a secondary graphite beam monochromator, a proportional Xe-filled detector, and a 35 position multiple-sample changer. The sample used for XRD measurements was not the same sample used for XRF and CT because, although in some cases XRD can be described as non-destructive, the sample was crushed to obtain qualitative diffraction peaks. The incident beam of the system was automatically collimated and the irradiated length was 12 mm. The secondary beam side comprised a 0.1 mm receiving slit, a soller slit, and a 1° antiscaner slit. The tube was operated at 40 kV and 30 mA. The XRD data were collected in a theta, 2-theta geometry from 0° to 60° with a step size of 1.20° 2-theta, a 2-theta resolution of 0.02°, a 2-theta counting time of 1 s per step. The semiquantitative interpretation of the diffractogram was done using X’Pert HighScore software. Semi-quantitative analysis calculates the estimated mass fractions of the accepted phases, based on scale factors and reference intensity ratios from a database. Meaningful results are obtained when all phases present in the sample are identified. If this is not the case, relative mass fractions of the identified phases are still reliable. As a consequence, error margins are not determined, but can be estimated to be in the order of magnitude of the detection limit, which is \(~1\%\). In this context, it must also be noted that XRD analysis is performed on a small sample compared to the average crystal size, resulting in an additional statistical error.

### RESULTS

#### XRF Mapping

For both the unpolished and the polished side, a 2D image of the total counts is generated for each element found in the object from the raw XRF spectra. A selection of these elemental mappings of the unpolished side is given in Figure 3 (note that each image has its own scale). Other elements found are Na, S, Cr, Rh, Sr, Y, Nb, La, and Ce, although most of these mappings are very noisy. It can be seen that for most elements the image is dominated by two or three homogeneous areas with different intensities.

Cluster analysis of the mapping of the unpolished side resulted in seven different clusters, as shown in Figure 4. The first cluster groups the pixels outside the granite cylinder, with low intensities for all elements. However, the upper right corner is incorrectly marked due to a shadowing effect caused by the source-detector geometry in the Eagle III sample chamber. Cluster 2 combines the Fe-rich regions containing Mg, while the Fe hotspots are grouped in cluster 3. Cluster 4 shows the Ti-Mn hotspots that also contain Fe. Regions with high Al and K intensity form cluster 5, whereas Al-rich regions with low K but high Ca intensity are united in cluster 6. Finally, cluster 7 is composed of regions with very high Si intensity. Small inclusions such as Zr hotspots are not included in the cluster analysis, but can be directly seen on the mapping.

Similarly, a cluster analysis of the polished surface was performed to verify the results of the 3D identification. The same clusters resulted...
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from the analysis, with a supplementary division of the Al-rich with low K intensity regions, based on the Ca intensity. Again, cluster 1 is the outside region, containing low Ca concentration caused by the blu-tack, the adhesive used to attach the sample to the sample holder. Cluster 2 and 3 are, respectively, low and high Fe intensity, corresponding to biotite and magnetite. Cluster 4 is ilmenite (Ti-Mn hotspots) and clusters 5, 6, 7, and 8 correspond to orthoclase, anorthite, albite, and quartz, respectively. Na was not taken into account for the cluster analysis because of the high noise level, but it corresponds well with the albite cluster. Contrary to the cluster analysis of the unpolished side, Mg was not taken into account and corresponds to cluster 2 except at the edges of cluster 3, where the consequences of the partial volume effect can be seen.

Identification

One of the more traditional methods to identify minerals inside a rock sample is the use of the polarization microscope. The different minerals described in the Yellow Rock are recorded in a thin section and images are acquired with a digital camera attached to a polarization microscope (Olympus 100× magnification). Figure 5A shows the main minerals of the Yellow Rock granite: anhedral quartz (2–4 mm diameter) and anhedral to subhedral plagioclase and K-feldspar. In some cases, alkali feldspar and orthoclase form narrow lamellae due to perthitic intergrowth (Fig. 5A). The lenticular exsolution lamellae inside the simple twin of orthoclase are between 5 and 80 μm thick. The secondary minerals are biotite (Fig. 5B) and opaque minerals such as magnetite. Other minerals like muscovite, converted potassium rich feldspar, and zircon, associated with some of the larger magnetite minerals (Fig. 5C), have a more sporadic occurrence.

Polarizing-microscope analysis mainly provides qualitative mineralogical information. Quantitative data in 3D can be obtained from 2D thin sections by interpolation using stereological methods, resulting in a statistically and not individually described mineral population (Jerram and Higgins, 2007). With constantly improving computer processing and modeling, the crystal size distribution and modal abundance can be closely approximated based upon thin sections, but true 3D information cannot be obtained. Other techniques like serial sectioning (Bryon et al., 1995) give direct 3D information, but are time-consuming and destructive. There is a need for techniques that deliver a chemical element and mineral distribution inside objects in 3D in a fast and nondestructive manner, especially for more complex objects.

X-ray diffraction (XRD) examines the crystallographic structure of a sample with the aid of X-rays. In contrast to thin section petrography, XRD examines a larger volume of the rock sample by comparing diffraction data against a database, but does not provide dimensional information either. Minerals absent in thin sections can thus be revealed by the latter technique. The diffraction pattern of the Yellow Rock sample is presented and interpreted in Figure 6.

Figure 5. Microscopic images of the Yellow Rock sample. (A) Lenticular exsolution lamellae of albite (Al) inside a simple twin of orthoclase (Or). (B) Biotite (B) and magnetite (M) in a quartz (Q) and plagioclase rich matrix. (C) Zircon mineral (Zr) in high positive relief.

Figure 6. XRD pattern of the Yellow Rock granite. Some of the mineral peaks are indicated (orthoclase [Or], biotite [B], albite [Al], quartz [Q], anorthite [An], zircon [Zr], ilmenite [Il], magnetite [M], and muscovite [Mu]).
By combining the XRD analysis and the microscopic investigation, eight different minerals could be identified in the sample. The three main components are quartz, orthoclase, and plagioclase, which make up more than 95% of the total volume. Biotite, ilmenite, magnetite, muscovite, and zircon make up a very small percentage of the analyzed sample.

Based on this information, the clusters found in the XRF analysis can be identified. It is clear that cluster 7, which contains a high Si concentration and no other elements, represents quartz (SiO₂). Cluster 3, the Fe hotspots, can be identified as magnetite (Fe₃O₄), while cluster 2 containing Mg and a relatively low Fe concentration is associated with biotite [K(Mg,Fe)₂(AlSi₃O₁₀)(F,OH)₂]. The Al-rich cluster with high K intensity (cluster 5) is believed to be the orthoclase (KAlSi₃O₈), while high Al concentration without K in cluster 6 indicates the presence of plagioclase feldspar, confirmed by the Ca mapping (anorthite, CaAl₂Si₂O₈) and the Na mapping (albite, NaAlSi₃O₈), although the latter is very noisy. Ti and Mn (cluster 4) can be found together in small ilmenite (FeTiO₃) spots.

**3D Segmentation and Visualization**

On the 3D volume resulting from the high-resolution CT scan, different phases can be distinguished based on the gray values representing their attenuation. As will be discussed later, this segmentation is disturbed by noise and partial volume effects. The histogram of the gray values is given in Figure 7, showing very few distinct peaks. The resulting phases can be analyzed and visualized in 3D. In Figure 8A, a view on the unpolished surface of the granite sample is shown: different clusters can be differentiated in the CT data and are segmented and given a color. Based on the information obtained from XRF and XRD, the green structures are identified as magnetite, and the blue ones as ilmenite. Yellow represents biotite and the purple dots are the densest particles corresponding to the Zr hotspots. Figure 8B represents the same analysis in the 3D sample through an arbitrary cut.

**Comparison of Mineral Abundances**

For the segmented phases, their volume fractions were calculated and compared to the XRD results. Due to the large range in composition of feldspar, there is no possibility for these minerals to be segmented in the μCT data (Figs. 7 and 9). Furthermore, quartz cannot be distinguished from albite. XRD resulted in 31% albite, 22% quartz, 18% orthoclase, and 16% anorthite. The volume fraction of biotite was found to be 0.82% ± 0.43% in the μCT data, but 2% in the XRD analysis. Other minerals represent a much smaller volume fraction, such as magnetite (0.38% ± 0.13% in the μCT data), ilmenite (0.28% ± 0.14%), and zircon (0.0461% ± 0.0023%), and are below the detection limit of XRD. It must be noted that the statistical error on magnetite and ilmenite is very large, caused by the small difference in attenuation between these two phases. This is confirmed when both phases are segmented together, resulting in a volume fraction of 0.668% ± 0.041%.

**DISCUSSION**

**3D Phase Segmentation**

As stated earlier, segmentation of the different minerals based on their gray values is not unambiguous. Since the attenuation coefficient depends on both density and atomic composition as well as X-ray energy, some minerals have...
very similar attenuation coefficients and it will thus not be possible to discriminate them with μCT. This attenuation coefficient can be theoretically calculated based on the NIST XCOM database (http://physics.nist.gov/PhysRefData/Xcom/Text/XCOM.html). For the minerals found in the Yellow Rock sample, the results are shown in Figure 10. It is clear that albite and quartz have very similar attenuation coefficients, as well as anorthite and orthoclase. However, most minerals found in igneous rock are solid solutions, of which the real composition and density are somewhat in between those of the two end members. Thus the attenuation coefficient of plagioclase minerals will be intermediate between that of albite and anorthite. Similarily, biotite is a solid-solution series between the iron end-member annite and the magnesium end-member phlogopite. In Figure 10, only annite is shown to improve image clarity. The biotite minerals present in the Yellow Rock sample contain magnesium as seen in the XRF mappings. The attenuation coefficient of phlogopite is almost equal to the attenuation coefficient of orthoclase and anorthite. Combined with the noise level, both phases have a very large overlap in the histogram. Consequently, biotite is hard to distinguish from these two other minerals, stressing the need for complementary research methods in order to identify the phases in the tomographic data.

Another effect that hinders good segmentation is the partial volume effect. This is caused by features that only partially fill the smallest 3D element, resulting in an averaged value for this voxel. The partial volume effect makes it very difficult and operator-dependant to segment the intermediate phases, particularly for samples with a high complexity and heterogeneity such as igneous rock. In the case of the Yellow Rock, the small lenticular exsolution lamellae of albite inside the orthoclase twins are increasing the partial volume

Figure 9. A 3D rendering of the original gray values on the unpolished surface of a Yellow Rock granite sample.

Figure 10. Linear attenuation coefficients of several minerals found in the Yellow Rock granite. Phlogopite has been left out for clarity. Note that some minerals have an intermediate composition between the two end members of the series.
effect. The presence of various trace elements in some of the minerals also results in complex and inappropriate segmentation.

One of the main issues in 3D data analysis is the thresholding step involved. Particularly in complex structures such as igneous rock, automated thresholding will not work and human intervention is necessary. However, this manual thresholding is operator-dependent and is as such liable to human errors, which cannot be quantified. Furthermore, segmentation was not obtained through simple thresholding, but a combination of dual thresholding, binary operations for the removal of noise and manual removal of wrongfully identified regions. Error margins were approximated by calculating the statistical error obtained when the same analysis was performed three times independently.

Cluster Analysis

Due to the relatively low spatial resolution of the μXRF mappings, some pixels contain different mineral phases and consequently contain averaged intensities. This is especially the case for the smaller minerals such as zircon, magnetite, and ilmenite. Furthermore, as the measured XRF lines originate from a greater depth compared to SEM-EDX analysis, subsurface heterogeneities at depths of several microns can contribute to the measured XRF mappings. The intensity of such a subsurface signal depends on the thickness or depth of the feature. If a mineral is covered by a very thin layer (relative to the information escape depth of the fluorescent X-ray) of another mineral, the chemical elements present in the covered mineral will still be measured.

The cluster analysis can be compared with the 3D rendering of the segmented phases. The identification was based on the unpolished surface, but should remain correct for the polished surface and can thus be verified. The result can be seen in Figure 11, where the ilmenite (dark blue) can be associated with cluster 4, and magnetite (green) can be correlated with cluster 3. The biotite (yellow) is more abundant in the 3D rendering (Fig. 12) than in the cluster analysis (cluster 2). The large cluster in the lower-left quadrant is falsely identified as biotite, but based on the XRF cluster analysis it should be associated with orthoclase. This interpretation error is caused by the identification based on the phlogopite, which has an attenuation coefficient very similar to the one of orthoclase. This problem can be solved by manually removing the objects in Morpho+ that have a very noisy nature such as the falsely identified biotite phase.

The lamellae seen in the optical microscopy (Fig. 5A) can also be resolved in the CT data (Fig. 13), but not in the XRF mapping due to its lower resolution. These structures will, however, lead to partial volume effects in these clusters, explaining the different intensities of K that can be seen in Figure 2, even though both regions contain the same mineral.

Limitations and Advantages

All three techniques, μCT, μXRF, and XRD, have very specific limitations and advantages. Due to the nature of the sample, more than 90% of the composition cannot be uniquely segmented in the μCT data. This is mainly caused by the complexity and solid solutions of the feldspar minerals, and the similar attenuation coefficient of quartz and the different feldspars. It is, however, possible to visually identify some structures on the reconstructed slices such as perthitic intergrowth. The μXRF results show a 2D map of the different clusters at the surface of the object. Although this shows clearly the main minerals, smaller structures cannot be identified by this low-resolution technique and partial volume effects become very dominant. Additionally, the solid solutions of the feldspar minerals prevent a correct identification of the minerals. These solid solutions are quantified separately in the XRD measurements, giving information on the abundance of the end members but not on the solid solutions themselves. On the other hand, the technique gives no spatial information.

CONCLUSION

X-ray micro-CT (μCT) is a very powerful tool in characterizing geological samples. However, the technique provides limited chemical
information to fully identify the different phases detected in the tomographic reconstruction. One of the possibilities to solve this problem is using additional techniques such as micro-X-ray fluorescence (μXRF) and X-ray diffraction (XRD).

The first technique detects the abundance of chemical elements present at the surface of the sample at a spatial resolution down to 10 μm. Its main strength is the nondestructive nature of the technique. The latter technique identifies minerals present in the sample, but is destructive and offers no spatial resolution.

For nonvaluable samples, a combination of both techniques with μCT offers a great added value in identifying different minerals in the sample. However, in the case of unique samples, the combination of only μCT and μXRF can offer a valuable and nondestructive alternative.

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