AMORPH: A statistical program for characterizing amorphous materials by X-ray diffraction.

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Abstract

AMORPH utilizes a new bayesian statistical approach to interpreting X-ray diffraction results of amorphous materials. **[need some further detail here on model]**. The program simulates background patterns previously manually applied, providing reproducible results, significantly reducing inter- and intra-user biases. This approach allows for the quantification of amorphous and crystalline materials and for the characterization of the amorphous component, including parameters of centre of mass, width, skewness, and nongaussianity of the amorphous component. Results demonstrate the applicability of this program for calculating amorphous contents of volcanic materials and independently modelling their properties in compositionally variable materials.

Introduction

Quantification and characterization of amorphous materials in an important area of research in terrestrial and planetary sciences (e.g. Schmidt et al., 2009; Dehouck et al., 2014; Wall et al., 2014; Morris et al 2016; Zorn et al., 2017). Powder X-ray diffraction, although primarily a tool for characterization of crystalline materials, also provides a means to investigate amorphous materials (e.g. Rowe et al., 2012; Achilles et al., 2013). Like any polymer, X-ray diffraction of rocks/soils containing amorphous materials (e.g. volcanic glass, opal, and organics) produces a diffraction pattern which is a combination of the crystalline and amorphous phases. Recent studies have debated the nature of amorphous materials in planetary sciences (e.g. Schmidt et al., 2009; Dehouck et al., 2014), and a growing number of applications to terrestrial volcanics have presented an avenue of expansion for XRD methodologies for amorphous material analysis (Ellis et al., 2012; Kanakiya et al., 2017; Zorn et al., 2017). Here we present a new computer program, AMORPH, which utilizes bayesian statistics to determine the crystallinity, and characteristics of, partially crystalline materials from X-ray diffraction patterns.

Several techniques currently exist for the quantification of amorphous materials, however these each present their own limitations. The two most commonly used approaches in recent literature either rely on a calibration curve for different crystallinities (calibration method; Rowe et al., 2012) or a combined Rietveld-Reference Intensity Ratio (RIR) method (Gualtieri 1996; Gualtieri, 2000). While the combined Rietveld-RIR procedure allows for quantification of both the amorphous and crystalline materials, for proper characterization it requires a library of pure components, spiked with a reference material (e.g. corundum). Sample spiking presents additional complications as it reduces the observed intensity of the amorphous material thus reducing the accuracy of pattern matching to determine abundances. An Excel based adaptation of this pattern matching technique (FULLPAT; Chipera and Bish, 2002) is utilized for characterizing remotely acquired X-ray diffraction patterns, such as those recovered from the Mars Science Laboratory (Bish et al., 2013). The problem faced by RIR approaches is they are based on modelling of an observed diffraction pattern compared to library measurements, and therefore do not allow an independent assessment of the characteristics of the amorphous material. In comparison, the calibration method focuses solely on the quantification of the amorphous material, utilizing the integrated counts associated with the amorphous and crystalline componentry.

MC % = [Cpa]/[Apa + Cpa] \* 100

Where MC is measured crystallinity, and Cpa and Apa are the integrated peak areas for the crystalline and amorphous components, respectively (see Figure 5 of Wall et al., 2014). While its simplicity has made it advantageous, the calibrated methodology has been limited in that the quality of the results largely depend on the ability of the user to manually assign backgrounds for count integration, and can result in large inter-user variations. Although the point of the calibration curve is to reduce the inter-user variation, determinations still tend to be associated with higher user error (3-5 vol %). As every user must independently practice background fittings using the calibration method, the results ultimately are only as good as the user’s ability to manually model the data. In addition, this technique, while not constrained by a necessary library of diffraction patterns, also does not characterize the XRD properties of the amorphous material. This study presents a new approach using Bayesian statistics to automate background determination for the calibration method, removing inter-user and intra-user biases in the determination of crystallinity and peak characteristics for amorphous/partially amorphous materials, regardless of what they are.

**Methods [Brendon’s sections]**

**Applications**

*Crystallinity*

The AMORPH program calculates a measured crystallinity using the procedure described above. It should be noted that this procedure does not negate the need for calibration standards to translate measured crystallinity to a true crystallinity. This is an important step as different X-ray diffractometers will provide slightly different calibration curves (Fig. X). Differences between instruments largely reflect changes in background intensity and shape, particularly at low two-theta. Calibration standards can be easily created by mixing powdered minerals (e.g. olivine, pyroxene, plagioclase) with powdered glass in known proportions to simulate volcanic material of varying crystallinities (e.g. Rowe et al., 2012; Wall et al., 2014). Results of the AMORPH calculations show good agreement to calibration curves using the manual calibration approach (Fig. Y). The offset between the AMORPH and manual calibration methods in Figure X is consistent with the change in analyzed 2-theta range, 10-40° and 5-50°, respectively (Fig. Z). Since the broad peak for the amorphous material does not extend appreciably out of the range from 10-40° two-theta (for a Cu K source), peak integration outside of this range will decrease the relative contribution of the amorphous material (only peaks for crystalline material are outside this range).

*Amorphous Characteristics*

As discussed above one of the primary advantages of the AMORPH program is that it can independently model characteristics of the amorphous component. In particular, centre of mass, skewness, and nongaussianity are distinctive amongst different amorphous materials. To test this, we present amorphous characteristics of rhyolite and basalt glass picked from a Taupo pumice (73.5 wt% SiO2; P2166C; Barker et al., 2015) and a Kilauea basalt (51 wt% SiO2; KS08-108E; Wooten et al., 2009; Rowe et al., 2015), respectively. In addition, Mars Scientific Laboaratory CheMin reduced X-ray diffraction patterns for the Bagnold Sand Dunes (Gobabeb; Lapotre et al., 2017; Achilles et al., 2017) and Buckskin (Morris et al., 2016) localities, both which have significant amorphous materials, have been processed for comparison (CheMin data publicly available at pds-geosciences.wustle.edu/missions/msl/chmin.htm). MSL diffraction patterns have been recalculated from a Co K to Cu K X-ray source to be visually comparable to terrestrial examples analysed for this study. Results are summarized in figure A. The most notable differences in diffraction patterns calculated between amorphous basalt and rhyolite glass include a positive skewness and shift to lower two-theta values for the rhyolite glass compared to the basalt glass. Although, CheMin diffraction analyses were run on a different X-ray diffractometer from the terrestrial samples shown here, similar relative changes in amorphous characteristics can be observed in X-ray diffraction data from Mars. These results suggest a distinct change in the composition of the amorphous material. This interpretation, is consistent with prior published results which suggest that at the Gobabeb locality (Namib Dune, Bagnold Dune Field), the sample is dominated by a basaltic mineralogy, while at the Buckskin locality, the amorphous component has been calculated to contain ~77 wt% SiO2 (i.e. rhyolitic; Morris et al, 2016; Achilles et al., 2017).

**Conclusions**

The AMORPH program’s statistical approach to interpreting amorphous materials in X-ray diffraction patterns provide a new unique, unbiased methodology. **[bit here from Brendon on the statistical approach]**.

A significant outcome of this research is that it reduces intra- and inter-user variability by eliminating the need for manual background fitting, the largest source of error in the calibration methodology for quantifying the amorphous component. Results demonstrate that this approach 1) accurately reproduces values of known crystallinity and 2) is consistent with prior manual approaches to the calibration method. Quantification of the amorphous content however still requires a calibration curve to correct for x-ray absorption/emission in mixed materials.

In addition to the quantification of amorphous and crystalline components, the AMORPH program calculates statistical parameters of the amorphous component, including the centre of mass, width of amorphous component, skewness, and nongaussianity. However, characterization of the amorphous component requires no calibration and outputs show clear distinctions as a function of amorphous composition in the demonstrated examples of volcanic materials from both Earth and Mars.

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