

## Local atomic structure of Fontainebleau sandstone: Evidence for an amorphous phase?

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[1] Rocks are traditionally viewed as crystallite aggregates; in general the treatment of the composition and mechanical properties never includes solid non-crystalline components. Such glass-like materials are difficult to detect in small quantities by standard techniques (e.g., thin-section polarimetry, x-ray diffraction) but if they exist at critical locations (i.e. grain contacts) they could affect the behavior of rocks considerably. Neutron scattering measurements on a solid sample of Fontainebleau sandstone have shown clear evidence for the presence of an unexpected glass-like component. Atomic pair distribution function (PDF) analysis shows significant local structural deviations from pure quartz. These deviations appear as an excess of 5–10% of nearest neighbor (NN) Si-O and O-O bonds, which is consistent with a 5–10% volume fraction of vitreous silica. These measurements may provide significant information about the still-unexplained causes for the peculiar mechanics and dynamics of sedimentary rocks. *INDEX TERMS:* 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 5112 Physical Properties of Rocks: Microstructure; 5199 Physical Properties of Rocks: General or miscellaneous. **Citation:** Page, K. L., Th. Proffen, S. E. McLain, T. W. Darling, and J. A. TenCate (2004), Local atomic structure of Fontainebleau sandstone: Evidence for an amorphous phase?, *Geophys. Res. Lett.*, 31, L24606, doi:10.1029/2004GL021717.

### 1. Introduction

[2] Many consolidated sandstones stand out due to their unusual mechanical and acoustic properties. The grain bonds, and the volume near the contact where stresses are high (due to the small cross-section), are responsible for the peculiar nonlinear properties [TenCate and Shankland, 1996; Darling *et al.*, 2004]. Crystallographically the structure of these sandstones appears to be mainly quartz. Pure quartz, however, does not display the unusual properties observed in consolidated sandstones and a detailed picture of the short- as well as long-range structure is critical to a deeper understanding of the dynamic behavior of sandstone and many other sedimentary rocks.

[3] We chose neutron measurements because they provide the only approach to learn about the atomic/lattice properties

of large volumes of intact rocks due to the very high penetration depth and improved scattering from light elements over x-rays. This is particularly relevant to rocks, where the mechanical properties cannot be deduced from the properties of the component grains [Darling *et al.*, 2004]. Enhanced atomic structure information may also be gained from high statistics runs on these large, consolidated state samples.

[4] It is important to remember that most common crystallographic techniques (e.g., x-ray diffraction) can only reveal the long-range average structure of the material, since only Bragg scattering is used. Deviations from this long-range average structure manifest themselves in diffuse scattering present in the scattering experiment. A convenient way to study the short-, medium as well as long range order in materials is the Pair Distribution Function (PDF) method. The PDF method has its origin in the study of materials without long-range order such as glasses and liquids. More recently, the systems studied using the PDF method have been extended to disordered crystalline and nano-crystalline materials [Egami and Billinge, 2003]. The pair distribution function,  $G(r)$ , describes basically the probability of two atoms being separated by a distance  $r$ . The function  $G(r)$  is obtained via the Fourier Transform of the total diffraction pattern as indicated below,

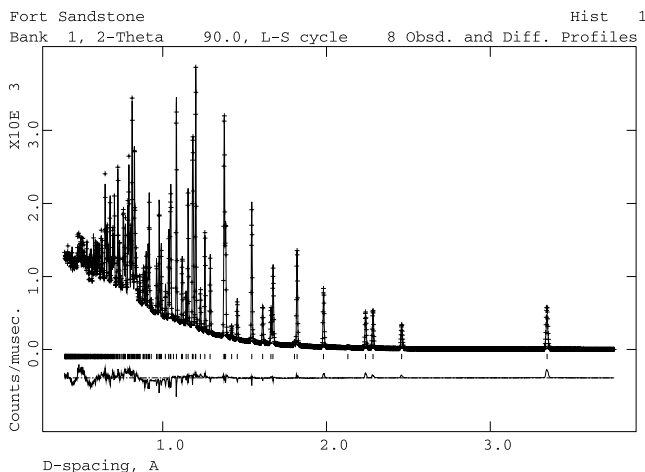
$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ \quad (1)$$

where  $Q$  is the momentum transfer ( $Q = 4\pi\sin(\Theta)/\lambda$ ) and  $S(Q)$  is the normalized structure function determined from the experimental diffraction intensity [Egami and Billinge, 2003].

[5] In this paper we use neutron PDF analysis to investigate the short- as well as long-range structure of an intact sample of Fontainebleau sandstone and show some interesting, unexplained deviations from pure crystalline structure suggesting the presence of a glassy phase.

### 2. Experiments

[6] The solid Fontainebleau sandstone sample was cored from a large rock quarried near Paris, France. The composition was obtained via X-ray diffraction from a powdered piece of the same rock. This sandstone sample is more than 99% quartz, with trace amounts of calcite, hematite, and



**Figure 1.** Rietveld results for Fontainebleau sandstone.

possibly feldspar. The sample grains are roughly 100–250 micron in size. The porosity of the sample is  $24 \pm 0.5\%$  and individual grains are bonded at several point-like contacts. A cylindrical piece of this sandstone, approximately 50 mm high with a diameter 9 mm was sealed in a vanadium can for the experiment. Neutron powder diffraction data were collected at ambient conditions on the Neutron Powder Diffractometer (NPDF) [Proffen *et al.*, 2002, 2003] at the Manuel Lujan Neutron Scattering Center of Los Alamos National Laboratory. This instrument was recently upgraded and optimized for PDF studies of disordered materials. The total data collection time for this sample was 24 hours which resulted in an unprecedented level of quality of the collected data.

[7] The PDF was obtained from the diffraction data using the program PDFgetN [Peterson *et al.*, 2000]. A cut-off in  $Q$  was introduced at  $40 \text{ \AA}^{-1}$  at which point the signal to noise ratio became unfavorable. This rather high cut-off results in a very high real space resolution in the PDF. The experimental data were corrected for background scattering, incident neutron spectrum, absorption, and multiple scattering, and then normalized by the incident flux and the total sample scattering cross section to yield  $S(Q)$ .  $S(Q)$  was subsequently Fourier transformed using equation (1) to yield  $G(r)$ .

### 3. Results

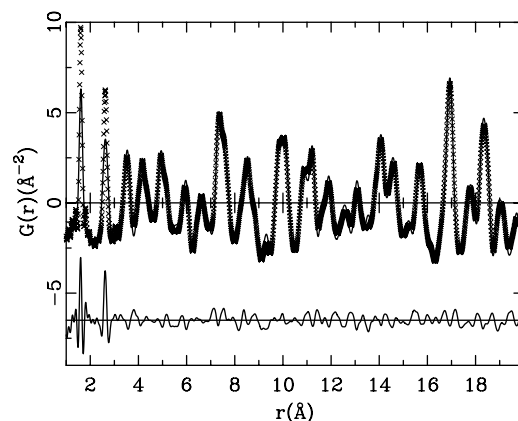
#### 3.1. Rietveld Refinements

[8] The Rietveld refinement analysis was performed with the GSAS package [Larson and Von Dreele, 1986]. The data was modelled with a crystalline quartz phase. The lattice parameters and atomic positions as well as isotropic thermal parameters were refined. The refinement result for

the 90 degree bank is shown in Figure 1 and shows excellent agreement. The model indexes all peaks and fits the data well, indicating there are no other long-range crystalline phases present in the sample. This is consistent with the X-ray diffraction result. We observe some modulations in the background visible in the difference curve shown in Figure 1. The resulting Si-O and O-O bond lengths are listed in Table 1. The neutron diffraction pattern does not contain any evidence for the trace amount of other minerals suggested by the X-ray analysis.

#### 3.2. PDF Analysis

[9] For the real-space PDF analysis, a crystalline quartz model with atomic positions taken from the Rietveld refinement was fit to the data. Refinements were completed using the program PDFFIT [Proffen and Billinge, 1999]. Initially, standard fitting was employed: lattice parameters, thermal parameters, scaling factors, and peak sharpening due to correlated motion were refined over a range of  $1 < r < 20 \text{ \AA}$ . Correlated motion is basically the tendency of near neighbor atoms to move in phase thereby sharpening the near neighbor PDF peaks. Details about correlated motion and its modeling in the PDF are discussed in Jeong *et al.* [1999, 2003]. The agreement was not as good as one would expect from a sample of pure quartz. This indicates some local deviations from the average structure. In order to investigate the nature of this disorder, various refinements of the PDF over different ranges in  $r$  were undertaken. One should keep in mind that the structural model is valid only over the range in  $r$  that has been refined. First we refined the PDF using a crystalline quartz model over the range  $1 < r < 20 \text{ \AA}$  (Figure 2). Two observations can be made from inspecting Figure 2: First the agreement for atom-atom distances with  $r > 3 \text{ \AA}$  is excellent. Second the agreement for the first two PDF peaks in the range of  $1 < r < 3 \text{ \AA}$  is rather poor. Apparently the first two PDF peaks in the model are somewhat broader compared to the experimental PDF. This is caused by the difficulty of obtaining a suitable value for the correlated motion parameter which requires a refinement over a large range in  $r$ . However, it is apparent that the integrated area under the PDF peaks is larger in the data than it is in the model PDF. The integral is proportional

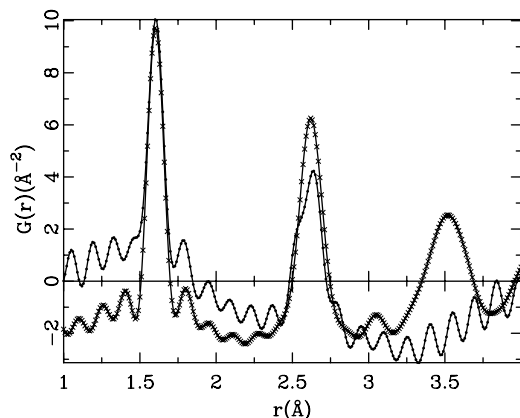


**Figure 2.** PDF of Fontainebleau sandstone with 1 to 20 Å fit model. The data are marked by crosses, the model by circles, and the difference curve by a line on a separate (lower) axis.

**Table 1.** Average Bond Lengths for Various Refinement Models<sup>a</sup>

Model	Si-O (Å)	O-O (Å)	Scale
Rietveld	1.611(3)	2.63(2)	-
3 to 20 Å PDF	1.611(3)	2.64(2)	1.119(4)
1 to 3 Å PDF	1.605(3)	2.62(2)	1.002(2)

<sup>a</sup>The number in parentheses gives standard deviation for the final digit of the bond lengths.



**Figure 3.** Nearest neighbor peaks for amorphous  $\text{SiO}_2$ . Sandstone data are marked with crosses while amorphous  $\text{SiO}_2$  data are marked with circles.

to the coordination number [Soper and Luzar, 1992] in the material, in other words there is excess Si-O and O-O nearest neighbor atom pairs which are not part of the crystalline quartz phase. We confirmed this by refining the PDF over the two ranges from  $1 < r < 3\text{Å}$  and  $3 < r < 20\text{Å}$ . In both cases we obtain a good agreement and the resulting Si-O and O-O bond lengths as well as the resulting scale factors for the PDF refinements are listed in Table 1. Interestingly, we find a significantly different scale factor for both refinements, which actually should be unity and independent of the fitting range in a single phase system. In fact the low  $r$  range refinement results in a scale factor of one, in other words in this range we account for all elements contributing to the scattering. For the refinement using the range  $3 < r < 20\text{Å}$  the calculated PDF needs to be multiplied with a larger scale to match the experimental values. All this points to the existence of excess Si-O and O-O bonds accounting for 5–10% of the material. Considering the size of the grains in the Fontainebleau sandstone and the amount of this excess phase, it is clear that the additional material can not be ascribed to disorder in a few atomic layers at the grain surface. A possible model is discussed in the next section.

### 3.3. Evidence for an Amorphous Phase?

[10] In speculating about the source of the extra Si-O and O-O bond contributions, other  $\text{SiO}_2$  diffraction patterns were examined. The PDF for amorphous  $\text{SiO}_2$  collected on NPDF is shown in Figure 3 as filled circles. It should be noted that the sample in this case was a fused silica tube measured as “background” for another experiment. Consequently the statistics are not nearly on the same level as the sandstone data. However, it is immediately apparent that the short-range structure is very similar to the Fontainebleau sandstone data shown as crosses in Figure 3. This is of course to be expected, since the local structure consists of  $\text{SiO}_4$  tetrahedra in both cases. Notice that there are only two sharp structural peaks in the spectrum of amorphous silica and they appear in Figure 3. Consequently, the Fontainebleau PDF data could be understood as a two phase system consisting of the crystalline phase and an amorphous silica phase.

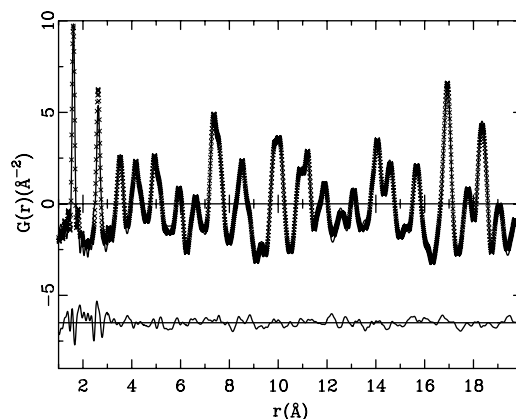
[11] To further investigate this idea, we refined a simple two phase model using PDFFIT. Both phases were structur-

ally derived from the single phase model result. However, the ‘amorphous’ phase was only contributing correlations up to  $r_{\text{max}} = 3\text{Å}$ . Structural parameters as well as a scale factor were refined for each phase. The refinement result is shown in Figure 4. One can see a much improved overall agreement. Nonetheless, the low  $r$  region is in need of further improvement. It is likely that correlated motion correction used is too simple for rigid units such as the  $\text{SiO}_4$  tetrahedra. We find that the resulting phase fractions are somewhat dependent on the details of the modelling of correlated motion. However, in all cases resulting in a comparable agreement with the data we find a phase fractions of the amorphous phase of 5–10% consistent with the estimate given in the previous section.

## 4. Discussion

[12] The results presented in this paper clearly show one thing: There is a non-crystalline contribution structurally consistent with a volume fraction of 5–10% of amorphous silica in Fontainebleau sandstone.

[13] It has been observed that crystalline quartz can amorphize under stress [Kingma et al., 1993; Kailer et al., 1999]. The point like contacts between grains observed in the Fontainebleau sandstone ‘amplifies’ the stress due to the small area for transmitting force, so there is a likelihood that some significant volume in the region around the contact may have been permanently amorphized by pressure during the sedimentation and bond formation. The stress gradient is also high in this near-contact volume, which may produce strain broadening of diffracted peaks in applied stress experiments like Darling et al. [2004]. If, however, this region is amorphous, there will be no contribution to the Bragg peaks, despite large stresses and gradients. The authors will be examining previous data carefully for these effects at the 5–10% volume level. The difference in the mechanical and fracture/annealing properties of amorphous and crystalline silica in these high stress regions may be significant elements in the explanation of many peculiar macroscopic behaviors in consolidated sandstones. Further confirmation of this theory is required by studying other



**Figure 4.** Two phase modeling for Fontainebleau sandstone. The data are displayed with crosses and the model is given by circles. The difference curve appears below the two data sets on a separate axis.

rocks of different crystal structures and/or grain sizes and porosity. In fact, the authors have undertaken a similar study on Berea sandstone, however in this case significant amounts of other minerals can be identified in the diffraction pattern. Although we find evidence for a similar amorphous phase in the Berea sample, the presence of structurally complex phases require much more careful modelling which is part of a future project.

[14] Finally it is worth pointing out that this example clearly illustrates the power of the PDF technique in characterizing materials with mixed crystalline and amorphous phases.

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