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^{57}Fe Mössbauer and X-ray characterisation of sandstones

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Abstract Sandstones from the Free State province in South Africa have been mined and processed mainly by small scale and artisanal miners in the rural areas. In the present investigation basic fire proof and water absorption tests, X-ray and γ-ray based characterisation techniques were used to study the sandstones. The collected samples were grouped according to their apparent colour in day light conditions and the elemental analysis showed the presence of a high amount of oxygen (>52%) and silicon (>38%) with Mn, Al, Fe and Ca as major elements in proportions related to the colour distribution of the various sandstones. The uniaxial compressive stress was found to be the highest (56 MPa) for the greyish sandstone and the lowest (8 MPa) for the white sandstone sample, also associated with the lowest (Al+Fe)/Si value of 0.082. The humidity test showed that the 6 % water absorption was lower than the recommended ASTM value of 8 %. The sandstone samples were also subjected to various high temperatures to simulate possible fire conditions and it was found that the non alteration of the mineral species might be one of the reasons why the sandstones are regarded as the most refractory amongst the building materials typically used. Mössbauer spectroscopy revealed that iron is present in all the sandstones, mainly as Fe^{3+} with the black sandstone showing an additional

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presence of 3 % Fe^{2+} indicating that a higher iron content coupled to higher silicon content, contributes to an increase in the uniaxial compressive strength.

Keywords Sandstones · Uniaxial compressive strength · (Aluminum+iron)/silicon ratio · Mössbauer parameters

1 Introduction

Sandstones in South Africa have been mined and processed mainly by small scale and artisanal miners commonly located in the rural areas. The sandstone samples that were studied in the present investigation are from the Free State province of South Africa which lies in the heart of the African Karoo Sequence of rocks, containing mudstones, shales, sandstones and the Drakensburg Basalt forming the youngest capping rocks [1–3].

The Free State province is high-lying, with almost all land being 1,000 m above sea level and some of the sandstones are resistant to weathering, yet easy to work, which makes them common paving and building materials. The sandstones occur in stratigraphic geological formations of sedimentary origin and have been found to contain fossils [4, 5]. They occur as arenaceous sedimentary rock types, composed mainly of sand-size mineral or rock grains. Most sandstones are comprised of mainly quartz and/or feldspar [1, 3]. Similarly to sand, sandstone varies in colour with the most common colours being tan, brown, yellow, red, grey, and white. Since sandstone beds often form highly visible cliffs and other topographic features, certain colours of sandstones may be strongly identified with certain regions [3]. Though the sandstone sedimentology study continues to focus on provenance, geology and environment, the diagenesis of sandstones has received renewed and intensive interest, especially from those interested in oil and gas or diagenetic mineral deposits. These materials constitute most important reservoirs for storage of valuable fluids [6]. Currently common usages of sandstones include building construction, decoration, wall fence paving, water retention and release in agriculture, and other cosmetic usages [2]. Miners, suppliers and end-users use the colours and textures observed, among the main deciding parameters for the application, sale and purchase, and mining, of this commodity. Its exploitation in South Africa is often indigenous and is practiced by family relatives and friends. Some small scale and artisanal entrepreneurs have constituted cooperatives and small business entities very often with little technical and material knowledge.

In the present investigation the aim is to use X-ray characterisation techniques in addition to ^{57}Fe Mössbauer spectroscopy to elucidate the intrinsic composition of the South African sandstone and correlate the mineralogical composition to the observed colour and mechanical properties.

2 Experimental

The sandstone materials used in this study were collected from the Free State Province of South Africa in the mountainous area of Qwaqwa (S-28^0 latitude and E-27^0 longitude – see also Fig. 1). The materials were studied using X-ray as well

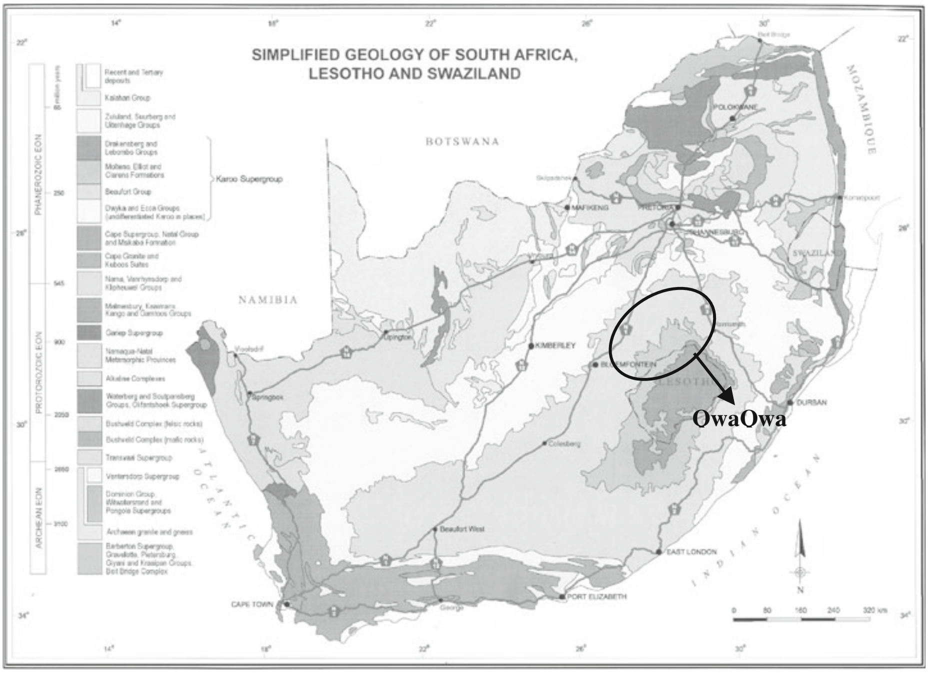

Fig. 1 Simplified geological map of South Africa showing the QwaQwa region where the samples were taken for this study [3]

as γ-ray based characterisation techniques. A Phillips X'pert model 0993 X-ray powder diffractometer (XRD) with Cu-K$_\alpha$ cathode was used for the identification of crystallites in the sandstone samples whilst a Philips Magix pro X-ray fluorescence spectroscope (XRF) was utilised to determine different elements present in the sandstones. A ^{57}Fe Mössbauer spectrometer was used at room temperature in conventional transmission geometry. The resonance profile was obtained by means of a Halder Mössbauer apparatus driven by a triangular reference wave form. A 50 mCi ^{57}Co(Rh) source transmitting 14.4 Kev resonant γ-ray radiation was detected by a Xe-filled proportional counter. The sandstone samples were ground to 75 μm and mounted in a $\varphi = 1.5$ cm sample holder where an average of 55–65 mg/cm^2 of sample formed a disk of uniform thickness for transmission Mössbauer measurement. A 25 μm thick ^{57}Fe foil was used for the velocity calibration. Prior to the analysis, each spectrum was folded and the spectra were fitted using the NORMOS fitting programme.

3 Results and discussion

The collected samples were grouped according to their apparent colour as observed in day light conditions and the following grouping was obtained: blackish, reddish, greenish, yellowish, and coarse grained whitish, shown from left to right in Fig. 2.

Fig. 2 From left to right the fine and compacted blackish, reddish, greenish, yellowish, and coarse grained whitish South African sandstone samples used in the present investigation

Table 1 XRF elemental analysis results of blackish, greyish, reddish, greenish, yellowish and whitish and South African sandstones

Sample	Blackish	Greyish	Reddish	Greenish	Yellowish	Whitish
Al	6.3	7.2	2.7	6.3	5.6	3.3
Ba	0.077	0.041	–	0.051	0.061	0.034
Ca	0.25	0.11	0.031	0.41	0.090	0.015
Cr	0.043	0.027	0.083	0.040	0.040	0.057
Fe	1.9	1.4	1.3	1.2	0.83	0.38
K	0.84	1.8	0.57	1.7	2.0	1.1
Mg	0.56	0.54	0.094	0.43	0.38	0.10
Mn	0.32	–	–	–	<<	<<
Na	0.94	0.89	0.14	2.3	2.4	0.078
Ni	0.12	0.079	0.24	0.13	0.11	0.17
O	54	52	56	54	53	55
P	0.048	0.045	0.010	0.025	0.017	<<
Rb	0.0051	0.0074	–	0.0069	0.0067	<<
S	0.0069	0.0062	0.013	0.0081	0.010	0.021
Si	41	38	46	40	40	45
Sr	0.0057	0.0060	<<	0.010	0.0086	0.0030
Ti	0.24	0.19	0.10	0.16	0.14	0.062
Y	0.0026	0.0021	–	<<	–	–
Zr	0.030	0.014	0.013	0.025	0.029	0.011
Co			0.14			
Cu			0.019			

<<: Below the detection limit

The elemental concentrations of the different sandstone samples, as determined by means of XRF analyses, are shown in Table 1. All the sandstones showed the presence of a high amount of oxygen (>52%) and silicon (>38%) with other major elements such as Al, Fe and Ca, in proportions related to the colour distribution from white to black. Manganese (Mn) was observed only in the black sandstone samples; however there was evidence of Mn traces in the yellowish and whitish sandstones.

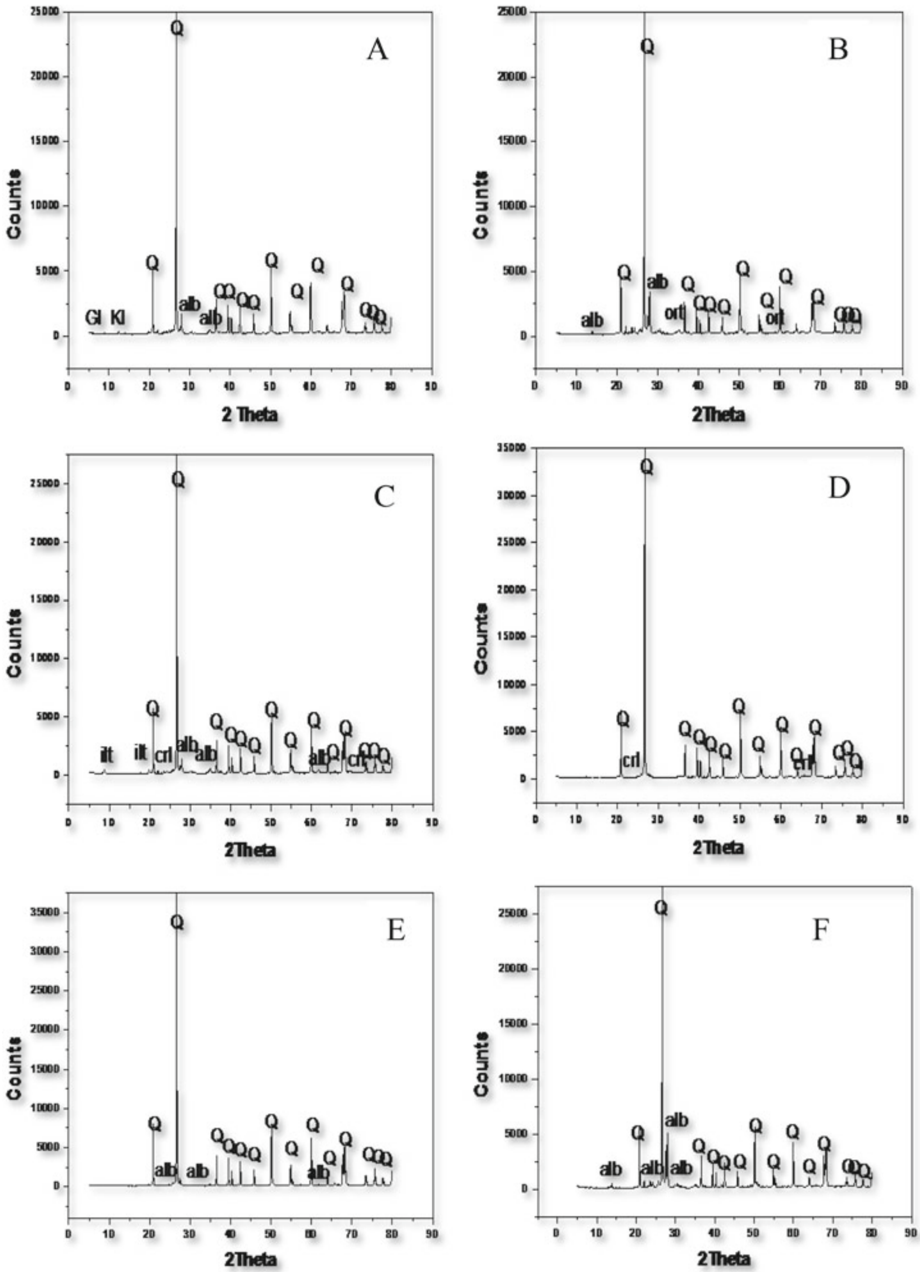

Fig. 3 XRD spectra of **a** (*blackish*), **b** (*greenish*), **c** (*greyish*), **d** (*reddish*), **e** (*whitish*), **f** (*yellowish*) sandstones showing the minerals identified (Q = quartz, alb = albite, Gl = Glauconite, Kl = kaolinite, ort = orthoclase, ilt = illite and crl=crysobilite

In agreement with the XRF results, the XRD analysis (Fig. 3) indicated that the sandstones mostly consisted of quartz (SiO_2), followed by feldspar minerals such al-

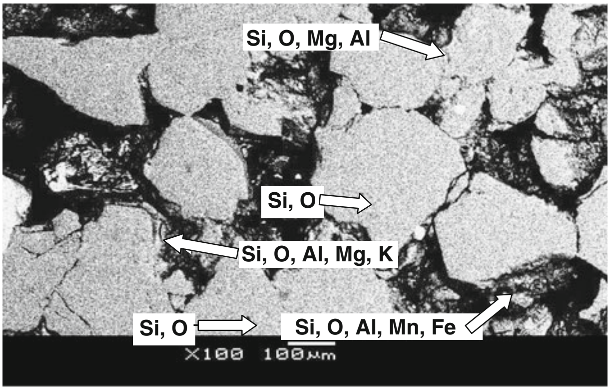

Fig. 4 Microphotograph of the blackish sandstone showing the morphology and the variation in chemical composition of the spotted grains respectively

Table 2 The Al, Si and Fe ratios and the uniaxail compressive strengths as found in the different sandstone samples

Sample	Blackish	Greyish	Reddish	Greenish	Yellowish	Whitish
Al/Si	0.15	0.19	0.06	0.16	0.14	0.07
Si/(Al+Fe)	5.00	3.96	11.5	5.33	6.22	12.22
(Al+Fe)/Si	0.20	0.25	0.09	0.19	0.16	0.08
Uniaxial compressive strength (Mpa)	16.03	56.74	22.79	26.27	9.42	8.23

Table 3 Room temperature Mössbauer parameters of the South African sandstones studied

Hyperfine interations parameters (mm/s)	Black	Greyish	Red	Green	Yellow	White
δ	$\delta_1 = 1.02 \pm 0.02$ $\delta_2 = 0.32 \pm 0.01$	0.33±0.01	0.30±0.01	0.31±0.01	0.34±0.01	0.05±0.02
Δ	$\Delta_1 = 2.66 \pm 0.03$ $\Delta_2 = 0.67 \pm 0.02$	0.60±0.02	0.62±0.01	0.56±0.02	0.56±0.02	0.02±0.01
Γ	$\Gamma_1 = 0.54 \pm 0.01$ $\Gamma_2 = 0.66 \pm 0.01$	0.75±0.05	0.85±0.05	0.76±0.04	0.64±0.03	0.81±0.09

δ = Isomer shift relative to α-iron, Δ = Quadrupole splitting and Γ = Width at half maximum

bite (Na,Al,Si_3O_8) and illite ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$. Other minerals, including glauconite ($(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$), kaolonite ($Al_2Si_2O_5(OH)_4$), cristobalite ($SiO_2$) and orthoclase($KAlSi_3O_8$) were identified at trace levels. Illite was only found in the blackish and greyish sandstone, kaolinite in the whitish and blackish sandstone, and orthoclase and sericite were found in only greenish and reddish sandstone (respectively) (Fig. 4).

The Si/Al ratio is often utilised to characterise sandstones according to their strength, with the relation to the sand grain size also of importance. Isomorphic substitution can occur between aluminium and iron in the octahedral sheet and thus aluminium and iron will be associated in the octahedral sites. The ratio of the Al-octahedral site to the Si-tetrahedral site (Table 2) is lower in the whitish sandstone compared to the other sandstones. This is perceived to be the reason for the low strength value (8.23 MPa) in the whitish sandstone (Table 2). In addition it should be mentioned that the whitish sandstone had the coarsest sand grains, which could

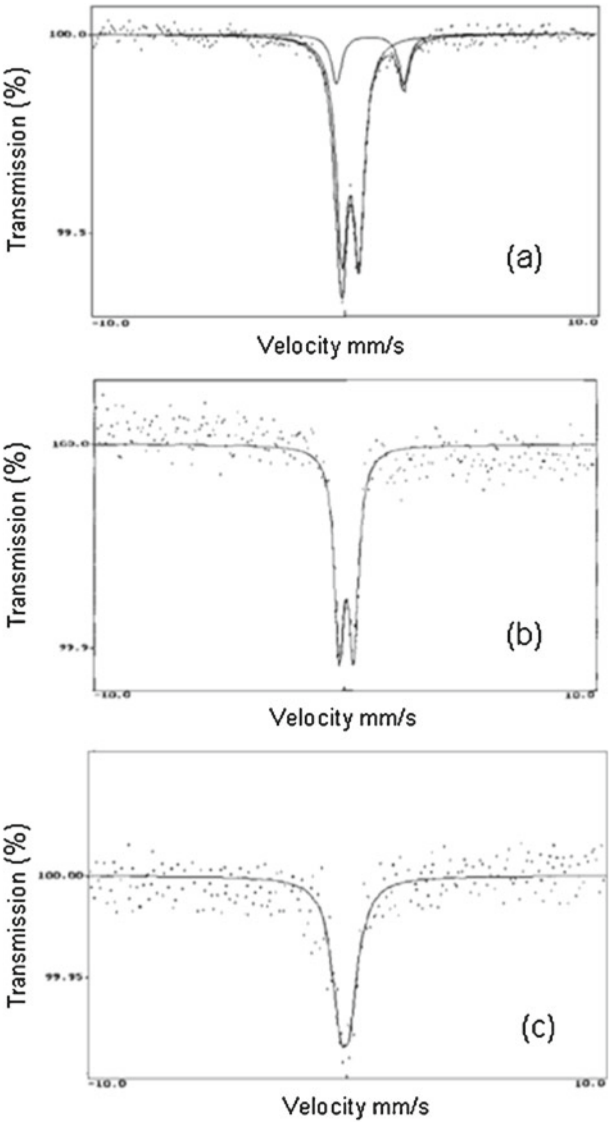

Fig. 5 Room temperature Mössbauer spectra of **a** *blackish*, **b** *greenish* and **c** *whitish sandstones*. The Fe^{2+}-compound was only identified in the black sandstones, with only a Fe^{3+}-component, in the octahedral environment, was found present in the *red*, *yellow*, *green* and *grey sandstones*

further lower the strength of the sandstone. The black sandstone on the other hand showed the highest amount of Fe present and it could be argued that higher iron content, coupled to higher silicon content contributes to an increase in the uniaxial compressive strength of that particular sandstone. The longitudinal compressive stress is then associated with the (Aluminium+iron) to silicon ratio and it was indeed found that the white sandstone with a (Al+Fe)/Si ratio of 0.082 (a factor of almost 3 lower that was found for the blackish sandstone) had the lowest compressive strength of 8.23 Mpa.

Mössbauer spectroscopy, (Table 3, Fig. 5) revealed that iron was present in all the sandstones investigated, mainly as a Fe^{3+}-component. The isomer shift and quadrupole splitting of the Fe^{3+}-component for the greyish, reddish, greenish and yellowish sandstones were similar (Table 3) with the parameters for the Fe^{3+}-doublet found in the coarse whitish sandstone being much smaller (Table 3). The black sandstones showed the presence of an additional 18 % Fe^{2+} and as mentioned, the higher amount of Fe present can increase the uniaxial strength, as shown in Table 2. The microphotographs also show the presence of iron in alumino silicate grains (Fig. 4).

The sandstone samples were subsequently immersed in water for 24 h and 48 h then air dried to determine the water absorption capacity. It was observed that the percentage of water adsorption was more or less the same for all samples and around 6 % (for both immersion durations and except for greyish sandstone which was 2.7 %). This is in compliance of the required less than 8 % amount as put down by the American Society for Testing and Materials (ASTM) standards. The whitish sandstone was found to have absorbed more water in 24 h than in 48 h, ending with the sample to break up completely. These characteristics will define whether a given colour sandstone material can be used for building, cladding, paving, flooring or decoration.

The yellowish and greenish sandstones were heat treated at different temperatures of 200 °C, 450 °C, 900 °C; 300 °C, 600 °C and 800 °C respectively, as a simulation of a case of fire in a building. It was found that quartz, as the major composition, did not easily altered under heat with only a decrease in the intensity of its peaks observed. The non alteration of the mineral species might be one of the reasons why sandstones are regarded as the most refractory amongst the building stones used.

4 Conclusion

In general the sandstones had similar morphological structures due to the fact that the sandstones share the same stratigraphic environment, with only the stratum of the sandstones influencing the grain size, ranging from fine-grained to coarse-grained, with the whitish sandstone being coarse-grained, the greyish sandstone being medium grained and the yellowish sandstone fine grained.

The results obtained for the chemical and mineralogical analysis seemed to correlate with each other and quartz was found to be the main constituent in all samples. As quartz is known for its hardness as sedimentary mineral, this is a good indication that the sandstones might be used in construction, although the colour, texture, hardness and water absorption will influence the type of construction it might be used for. The sandstones were found to have a low iron content where iron is known for mobilization and deforming sandstone buildings through exposure to rainfall over a certain period. The red, yellow and green sandstones are desirable to be used in buildings, however if the sandstone is weak in strength and absorbs too much water then it can't be used and it can then only be used for cladding and decorations. The sandstones were found to absorb less water than the ASTM standards of less than 8 % and are thus all fit for various uses. The compressive strength of the greyish and greenish sandstone was found to be good and the whitish sandstone was found to exhibit the lowest strength and it would thus not be fit as a building material.

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References

1. Viljoen, M.J., Reimold, W.U.: An Introduction to South Africa's Geological and Mining Heritage, The Geological Society of South Africa and Mintek, 1st Edition, ISBN 0 86999 941 9, p. 193 (1999)
2. de Jager, F.S.J.: Mineral resources of South Africa. In: Coetzee, C.B. (ed.) Dept. of Mining and The Geological Survey of South Africa, 5th edition, ISBN 0 621 03465 7, p. 462 (1976)
3. Norman, N., Whitfield, G.: Geological Journeys, Struik Publishers, South Africa, ISBN 1 77007 0621, p. 320 (2006)
4. van Dijk, D.E.: Taphonomic aspects of the Wagondrift Quarry site and their implications for the depositional environment of the upper Permian Estcourt Formation. S. Afr. J. Geol. **114.2**, 105–109 (2011)
5. MacRae, C.: Life etched in stone – Fossils of South Africa, Geological Society of South Africa, 1st Edition ISBN 0-620-23388-5, p. 305 (1999)
6. http://www.equities.com/news/headline-story?dt=2012-11-16&val=721733&cat=energy. Accessed 16 Nov 2012