Macroscopic Ferronematic Liquid Crystals Determine the Structure of Kimberley Zebra Rock

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Observations on zebra rock (KZR) from the Kimberley area, Western Australia, show that the kaolinite and hematite particles in KZR have a common preferred orientation. We show that the striking and diverse features of its banding can be explained as a relic of a Precambrian liquid crystal phase of centimetre dimensions. This is the first report of a discotic ferronematic and of a Freédérickzs transition in a geological formation.

1. Introduction

Zebra rock (KZR) from the Kimberley area, Western Australia is remarkable for its patterns of red-brown bands and rods against a white background (Fig. 1). Attempts to explain its origin in terms of sedimentation processes and Liesegang banding have been summarised by Loughnan and Roberts [1]. However none of these processes can explain the bands' generally regular spacing, width, occasional forking into two bands or evolution into rods or ellipses. They also do not explain the frequent edging by a band at a large angle to the red and white pattern. We propose an explanation in terms of a ferronematic Precambrian liquid crystal (LC) phase.

2. Results

XRD and SEM analysis verified that the principal mineral constituents [1] of KZR were quartz, SiO_2; kaolinite and dickite polytypes of $Al_2Si_2O_5(OH)_4$; sericite or white hydrous muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$; and hematite, α-Fe_2O_3. Most of the hematite was in the red-brown zones. A sketch of the principal specimen studied is shown in Fig. 2. The SEMs revealed kaolinite platelets, preferentially oriented with the normal to the platelets along the X direction. The hematite particles were irregularly shaped. A parallelepiped section was cut from the right-hand side of red-brown band 1 in Fig. 2, and XRD spectra were taken with the beam incident on each of the XY, YZ and ZX planes. Preferred orientation was evident and the intensity ratio, R, of the (001) kaolinite reflection to the (110) reflection was calculated (Table 1). The expected ratio for random kaolinite powder (p) is $R_p = 2.5$, so the results were normalised to produce an orientation parameter (OP):

$$OP_i = (R_i - R_p)/R_p,$$

where the subscript i refers to the X, Y or Z axis. A positive OP value represents a preference for the normal to the basal plane, [001], to point along i. Table 1 shows that this preference is along, or near to, the X direction. A similar analysis was done for the hematite peaks using the (104) hexagonal reflection to characterise the basal plane because of the difficulty in measuring a clean (00ℓ) reflection as used for kaolinite. These results also showed (Table 1) a strong preference for the normal to the (104) plane to lie along, or near to, the X axis.

A section was taken of the full height of the sample along the left side in Fig. 2 and mounted so that an XRD spectrum was taken of the XY plane. Successive spectra were collected such that, after each spectrum, 0.9 mm was ground from the specimen and the next spectrum taken of the newly exposed surface. The value of OP_Z for kaolinite and hematite

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was calculated from the line intensities for each of the 66 spectra. It varied cyclically and was smallest (i.e. least ordered) at the centres of the red-brown bands for both minerals.

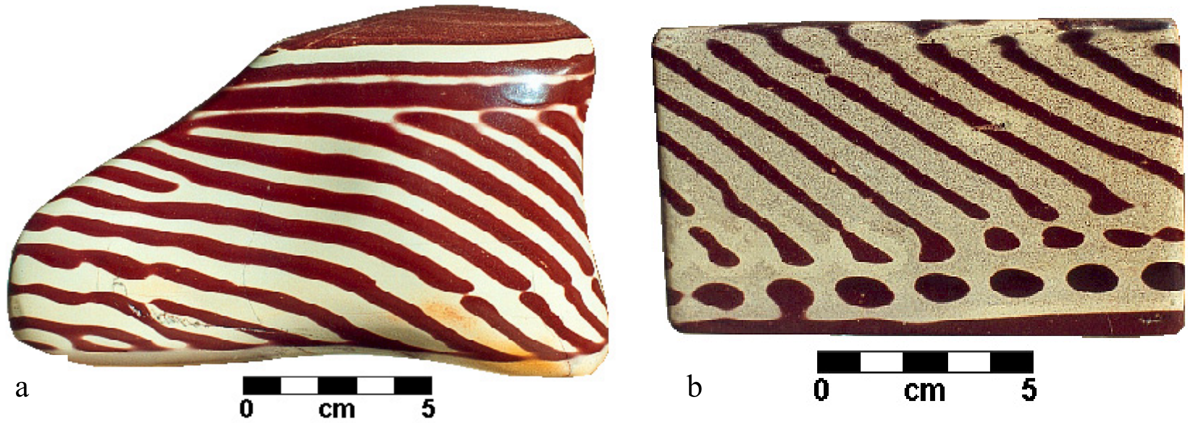

Fig 1. Specimens of Kimberley zebra rock: (a) bands approaching bounding red and white bands at changing angles and red dislocations in the centre left and lower left, (b) narrower red bands changing into ellipses near the boundary.

Orientation dependence was also observed in two of the EPR signals, one attributed to an $Al-O^{-}-Al$ centre in kaolinite and the other to one of the three sites in which Fe^{3+} substitutes for Al^{3+} in kaolinite. SEMs showed that the kaolinite platelets were ≈ 1-5 μm in diameter whereas the hematite particles were generally slightly smaller at 0.2-1 μm. A Mössbauer spectrum at room temperature showed a clear sextet of hematite above the Morin temperature, while spectra at 81 K and 5 K both showed that approximately 65% of the hematite had not passed through the particle size-dependent, Morin spin re-orientation transition. For pure hematite, the Morin transition temperature, T_M, is approximately 263 K in the bulk, and as the particle size decreases it is completely suppressed for particles of approximately 20 nm. The Mössbauer results suggest a bimodal particle size for the hematite.

3. Discussion

The LC attributes of clays have been studied since the 1930s and the platelet morphology of kaolinite forms a discotic nematic LC. In our model of the formation of KZR, we propose that this aqueous LC was infiltrated by a ferrous solution. The iron probably precipitated as ferrihydrite, which we have detected by EPR. A ferronematic was formed as the ferrihydrite transformed to the weakly ferromagnetic hematite, both of which share common growth habits with kaolinite [2].

Although hematite has a small uncompensated moment of 5.5 x 10^{-3} μ_B per iron atom for $T > T_M$, this is still large compared to the diamagnetic moments which drive molecular ferronematics. The Freédérickzs transition in ferronematics occurs due to competition between orientational edge effects, which dominate at the boundary, and the orienting effect of the magnetic field, which dominates in the centre [e.g. 3]. In synthetic ferronematics, the transition is usually triggered when the magnetic field reaches a critical value [4]. However, in KZR it will be triggered when the total magnetic moment exceeds a critical value. Applying the formula derived by Zubarev and Iskakova [5] for a ferronematic with rod-shaped particles, we find that a particle size of approximately tens of nanometre has sufficient magnetic moment to drive the transition in a field equal to the current value of the Earth's field.

Rod-shaped particles in a ferronematic can move sideways and lengthways and can rotate, all with relatively little hindrance. However, disc-shaped particles can neither move perpendicular to their plane, nor rotate about an axis in their plane, because of the constraints of their neighbours. As the size and magnetic moment per hematite particle increased, the dipole-dipole interaction causes them to aggregate by sliding sideways between the kaolinite platelets, creating the red and white banding. This requires that the LC director (i.e. the normal to the platelets) must lie in the plane of the bands, as observed in the XRD results.

Table 1. Preferred orientation values from XRD spectra for the sectioned parallelepiped from a red band.

Axis	Kaolinite OP_i	Hematite OP_i
X	3.0(2)	1.18(7)
Y	-0.67(5)	-0.59(4)
Z	-0.53(3)	-0.49(3)
Powder	0	0

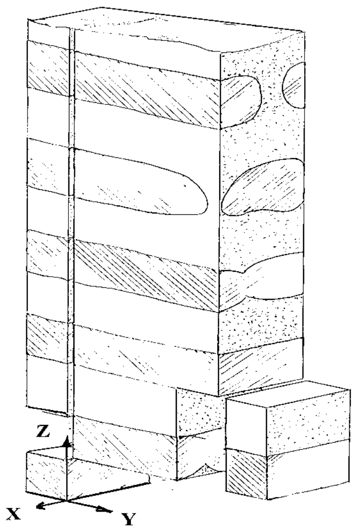

Fig. 2. Sketch of the regular bands in the principal sample studied, defining the axes used in the text. The period of the bands was approximately 1.2 cm.

Edge effects in LCs determine the director orientation and in KZR this is parallel to the edge of the enclosing strata. If the Earth's magnetic field is approximately parallel to the director, then planar bands are produced. However, if they are not parallel, the torque on the hematite will compete with the edge effects and produce the curved bands as seen in Fig. 1a, a splay mode in LC terminology. The theory of ferronematics can also explain the presence of edge dislocations (Fig.1a) and cylindrical red-brown zones (Fig. 1b) and thus appears capable of accounting for all the observed features in KZR.

It is concluded that Kimberley zebra rock preserves the texture of a liquid crystal from the Precambrian era. This is the first report of a Freédrickzs transition in nature and also the first observation of a LC with micrometre size particles and linear dimensions of tens of centimetres. The properties of model ferronematics can explain the patterns in KZR including the segregation of hematite into regular bands and rods, dislocations, the periodicity of the pattern, and variations in the angle between the bands and the sedimentation plane.

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