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ELECTRON MICROSCOPIC INVESTIGATION OF FE-RICH PHYLLOSILICATES

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Green glauconite-like minerals from Weipa, Australia, which were previously known as glauconite, were determined to be unusual Fe-rich vermiculite and Fe-rich smectite. This study revealed the structural and chemical nature of these unique phyllosilicates with HRTEM, AEM, SEM and XRD analysis.

The Fe-rich phyllosilicates comprising up to about 15 wt% of the rock occur with various amounts of quartz, mica, feldspar, low-Fe smectite, kaolinite, pyrite and siderite at about 30 meters depth in unweathered marine sediments of the Rolling Downs Formation at Weipa. The proportions of Fe-rich vermiculite and smectite decrease upward and become undetectable in the upper saprolite zone at about 23 m depth.

Two major morphologies of the Fe-rich phyllosilicates were observed. One is of tabular or granular detrital-shaped form (Fig.1a); the other is platy or film-like, coating grains and occurring in matrix and fissures (Fig.1b). The Fe-rich vermiculites, like other vermiculites, have a relatively macroscopic nature, occurring only as tabular grains, whereas Fe-rich smectites are present in both morphologies. Detrital-shaped grains often show a non-uniform chemical composition as seen in back-scattered electron images, comprising an interlayered mixture of Fe-rich vermiculite and Fe-rich smectite along the same crystallographic direction (i.e., z-axis) (Fig.1a). However, some grains were found that were chemically uniform; that is, consisting of Fe-rich vermiculite. Film-like Fe-rich smectites were found to occur as rosette clusters consisting of relatively flat plates (Fig.1b), whereas the low-Fe smectite has a corn-flake-like wavy morphology (plate boundaries are not clear). Identification of these phases in the SEM images was made by X-ray analysis.

The Fe-rich vermiculites were identified by HRTEM and electron diffraction on the evidence of straight 12-Å layers with the presence of a brucite-like interlayer and fewer defects than smectite (Fig.1c). Under the TEM, it is believed that one water layer out of two within the interlayers of vermiculite is lost, which results in the collapse of the basal spacing from 14-Å as observed in XRD to 12-Å. The Fe-rich smectites were texturally characterized as having relatively wavy 10- to 11-Å layers (Fig.2a), and illite by its having relatively defect-free straight 10-Å layers. The packets of Fe-rich smectite are thicker than those of low-Fe smectites (i.e., montmorillonite) along the z-axis. Low-Fe smectites are more bent and have a higher density of defects such as edge dislocations.

Based on elemental analyses by EDS on SEM and AEM, the Fe-rich vermiculite has the formula: $(Mg,K,Ca)_z(Fe,Al,Mg)_y[Si_{4-x}Al_x]O_{10}(OH)_2{\cdot}nH_20$, where x varies from 0.9 to 1.5, y from 2.0 to 2.8, z from 0.5 to 0.9. The vermiculite has a high Fe content (ranging from 1.1 to 1.9 in the above formula) in the octahedral sites. It differs from 'normal' vermiculite by having low Mg contents in the octahedral sites. Most Mg in the Fe-rich vermiculite is present as a major interlayer cation.

The Fe-rich smectite has the formula: $(K,Ca)_z(Al,Fe,Mg)_y[Si_{4-x}Al_x]O_{10}(OH)_2{\cdot}nH_20$, where $x \approx 0.9$, $y \approx 2.5$, $z \approx 0.3$. The smectite is dioctahedral and has Al as the dominant cation in the octahedral sites. Its Fe content (total Fe) is about 0.7 in the above formula and Fe/(Fe+Mg) ratio is about 0.67. The Fe-rich smectite has a high Al content in tetrahedral sites and a relatively high Fe content in octahedral sites, compared to montmorillite and beidellite. It differs from nontronite by having high Al contents in both tetrahedral and octahedral sites. Fig.2b illustrates the chemical distinctions between the unique phyllosilicates and other sheet silicates in the Si-Al-Fe+Mg composition.

The Fe-rich phyllosilicates in Weipa co-exist with authigenic pyrites, hence they formed in a reducing environment. Tabular crystals of Fe-rich vermiculite and smectite are interpreted to have formed by replacing detrital biotites rather than muscovites. Film-like Fe-rich smectites having less chemical variation are interpreted to be of authigenic origin. It is likely that the film-like smectites result primarily from authigenic crystal growth that begins with the precipitation of a poorly crystallized Fe-rich smectite that then evolves into a better crystallized phase. The Fe-rich phyllosilicates become unstable towards the surface due to weathering, and transform to low-Fe smectite, kaolinite, and iron oxyhydroxides. Fe-rich vermiculite has likely altered to Fe-rich smectite first during weathering process, then to low-Fe smectite.

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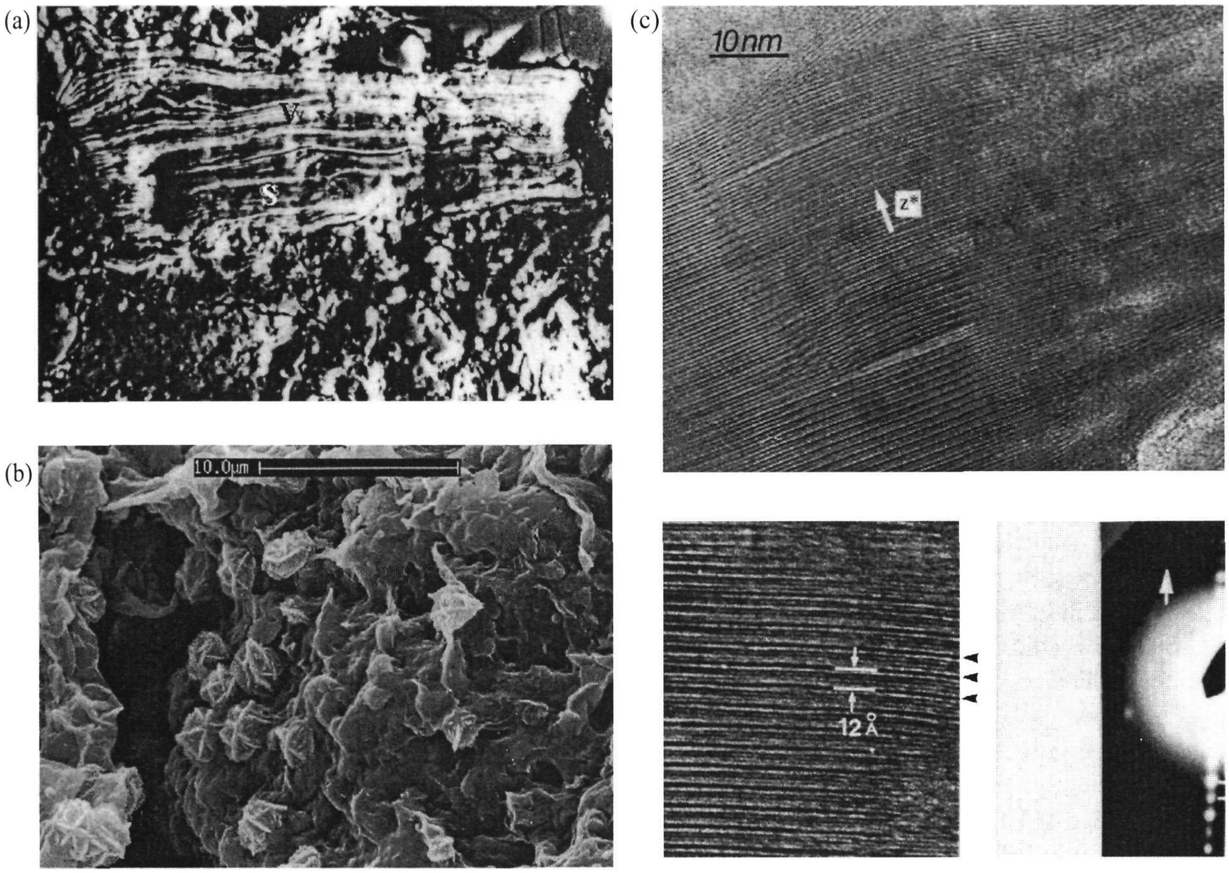

FIG 1. (a) BSE image showing detrital-shaped grain, bright bands are Fe-rich vermiculites (V), dark bands are Fe-rich smectites (S). (b) Secondary electron image showing relatively flat platy or film-like high-Fe smectites forming rosette clusters. (c) HRTEM images of Fe-rich vermiculite revealing the 12-Å basal lattice fringes and the brucite-like interlayers between the 2:1 layers as marked by black arrows, SAED pattern showing 12-Å spacing.

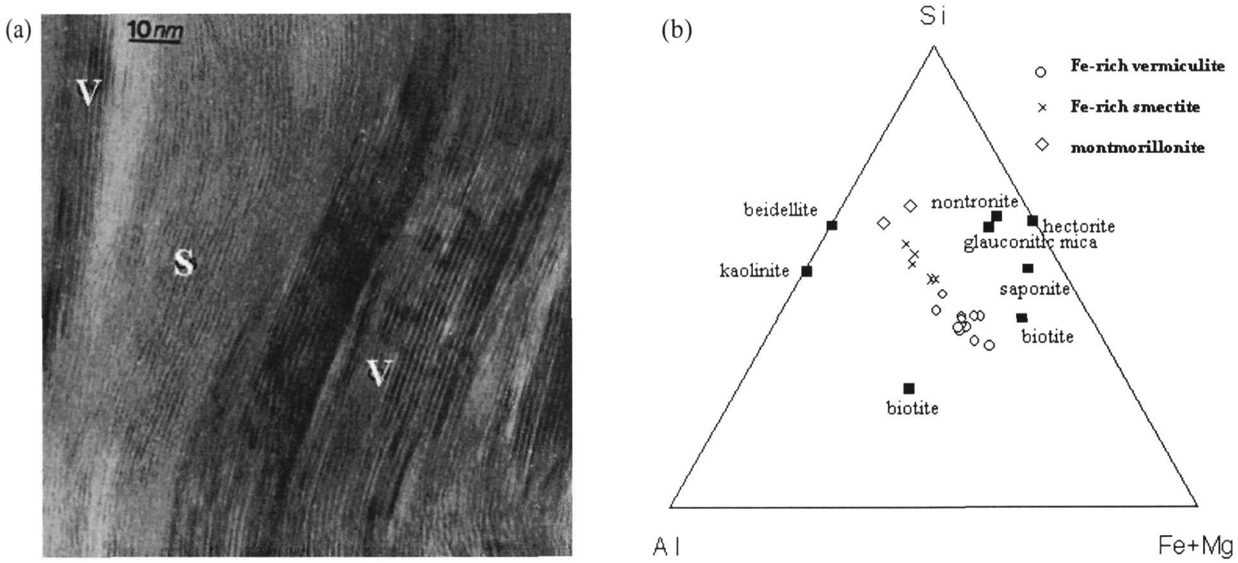

FIG 2. (a) HRTEM image showing the 10 to 11-Å fringes of Fe-rich smectite (S) associated with Fe-rich vermiculite (V). (b) Compositional comparison between Fe-rich vermiculite, smectite and other sheet silicates.