

Timing and Significance of Celadonite Alteration in Graphitic Schist on southern Eyre Peninsula, South Australia

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Abstract

Minor celadonite is associated with extensive nontronite alteration in deeply weathered graphitic schist and gneiss at the Uley graphite mine, 18 km southwest of Port Lincoln, and is a co-dominant alteration mineral, with silica, iron and manganese oxides, in sheared graphitic schist in coastal cliffs at Sleaford Bay, 7.3 km south of the Uley mine. The bluish-green clay mica was characterised using X-ray diffraction (XRD), chemical analysis and electron microscopy. Selected size fractions were dated by K-Ar method. Celadonite, replaces biotite and infills veinlets as crystalline micro-laths to 10 µm long by 1 µm wide and ~0.1 µm thick, of ferroceldonite composition $K_{0.82}Na_{0.03}(Fe^{3+}_{1.08}Al_{0.06}Fe^{2+}_{0.20}Mg_{0.55})Si_4O_{9.9}(OH)_{1.98}(H_2O)_{0.12}$. At Uley mine, celadonite is partially replaced by kaolinite. The timing of celadonite formation at Sleaford Bay was ~48 Ma (early Eocene) and at Uley mine ~16 Ma (early-mid Miocene). Celadonite alteration within granulite facies metasediments of the Paleoproterozoic Hutchison Group is unusual. These occurrences are interpreted to form from saline meteoric water in shear zones during local high sea level events, and at sites where earlier weathering of near-surface graphitic zones provided an environment in which electro-chemical effects, around graphite conductors, may have modified the oxidation potential and style of alteration.

Keywords: K-Ar dating, celadonite, silica lepispheres, cryptomelane, electro-chemical alteration, graphite

Introduction

Geological investigations during the 1990s at the Uley graphite mine, 18 km southwest of Port Lincoln, identified extensive nontronite alteration of graphitic schist and gneiss, and interlayered amphibolite (Keeling et al., 2000). The nontronite extends below the apparent base of weathering at ~60 m depth, and is modified at higher levels by kaolinisation. This may reflect successive weathering events under different environmental conditions, but from the weight of evidence it was concluded that the nontronite most probably was the result of a low-temperature hydrothermal event occurring post high-grade metamorphism that culminated during the Paleoproterozoic Kimban Orogeny (*ca* 1730-1700 Ma).

Minor patches and thin veinlets of dioctahedral, iron-rich mica, celadonite, were identified in the alteration zone at the Uley mine and subsequently recognised as more pervasive alteration in graphitic schist at Clem Cove on Sleaford Bay, ~7.3 km south of Uley. The occurrences are unusual in that celadonite most commonly occurs in hydrothermally-altered mafic volcanic rocks, often in mid-ocean ridges, and less commonly in terrestrial basalt flows and hydrothermally-altered or low-grade metamorphosed volcanic tuffs (Li et al., 1997; Baker et al., 2012). Celadonite contains K_2O ~9% and can be dated by potassium-argon analysis. Renewed interest in graphite exploration provided the incentive to date the celadonite alteration to assist with understanding its timing and distribution, and potential impacts on graphite grade and recovery. Described below, are the results of investigations on celadonite characterisation, timing of celadonite crystallisation, and preliminary interpretation of the environment of formation.

Geological Setting

Uley graphite mine is in granulite facies metamorphic rocks equated with Paleoproterozoic Hutchison Group metasediments, originally deposited as marine, fine-grained clastic and chemical sediments between 2000 and 1850 million years ago. Graphitic beds averaging 13% graphitic carbon were organic-rich marine clays and silts, essentially the accumulated remains of single-celled organisms. The sediments were intruded by mafic dykes and sills and were deformed and metamorphosed during the Kimban Orogeny, with peak metamorphic conditions estimated at 1000 Mpa and 730°C (Dutch et al., 2008). The Uley open pit mine is on the hinge of an anticlinorium that plunges to the north-northwest with graphitic schist and gneiss folded in a series of minor isoclinal folds, overturned to the east, with the synclinal limbs strongly attenuated by shearing along graphitic layers (Keeling, 2000). Nontronite alteration is broadly distributed in schist and

interlayered amphibolite, but celadonite is less common and occurs as small patches and veinlets in weathered, kaolinitic, high-grade graphitic schist in the eastern pit wall.

The Sleaford Bay occurrence is near the western end of Clem Cove in a 12 m-thick zone of sheared and highly altered graphitic schist and gneiss that strikes north-south, with schistosity dipping at 65-70 degrees to the west. The alteration is a mixture of celadonite, goethite, silica and manganese oxides. Bluish-green celadonite forms as thin stringers and as veins and patches, several centimetres across. The geological section in 20 m high cliffs at Clem Cove and adjoining Lone Pine Beach is a key exposure of Hutchison metasediments, described by Tilley (1921) and often revisited, most recently by Vassallo and Wilson (2001). East of Clem Cove, the Kalinjala Shear Zone (KSZ) juxtaposes Hutchison Group metasediments against the 1850 Ma Donnington Granitoid Suite (Fig. 1). The KSZ is a high strain zone, up to 6 km wide, that extends for 400 km along the eastern margin of Eyre Peninsula and is a major structure controlling metamorphic intensity and possibly crustal heat flow. It continues to be a focus of seismic activity.

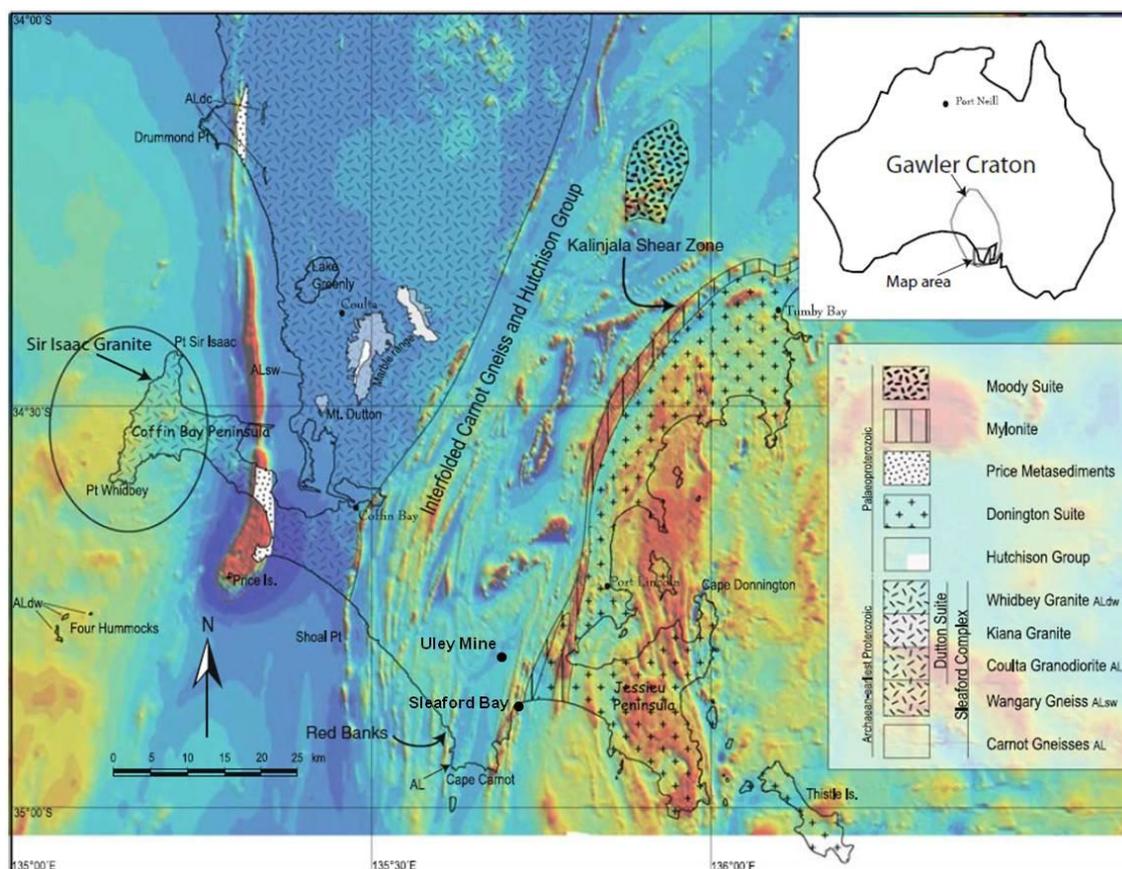


Fig. 1 Geology summary overlaid on regional magnetic background, showing celadonite locations Uley mine and Sleaford Bay (after Dutch et al. 2008).

Methods

Selected samples of celadonite-altered rocks were examined in thin section and by scanning and transmission electron microscopy. Handpicked, vein celadonite from Sleaford Bay was ground in a mortar and pestle and separated into size fractions $<0.2 \mu\text{m}$, $0.2\text{-}1 \mu\text{m}$, and $1\text{-}2 \mu\text{m}$ by ultrasonification and centrifugation, principally to reduce fine-grained goethite. The $1\text{-}2 \mu\text{m}$ fraction contained the least goethite, which was removed by cold sodium dithionite treatment. This sample was used for chemical analysis by X-ray fluorescence (XRF) analysis of a fused disc. The FeO content was determined by colorimetric method. Mineralogy by XRD was on pressed powders using Co K α radiation. For dating, two size fractions of Sleaford Bay celadonite were prepared at $0.2\text{-}2 \mu\text{m}$ and $1\text{-}3 \mu\text{m}$. For the Uley mine, the $2\text{-}5 \mu\text{m}$ fraction was separated for three samples (UGCE1, UGCE4, UGCZ) from celadonite patches in the eastern middle bench of the Uley open pit. Size fractions were chosen to maximise celadonite and reduce fine-grained kaolin and goethite. The mineralogy of the fractions was monitored using XRD. Potassium was determined by atomic absorption spectrometry, and Ar was extracted and measured after pre-heating at 100°C for ~ 12 h to reduce

atmospheric gasses adsorbed on the mineral surface during processing. Standard K-Ar decay constants were used for age determination.

Results

Replacement of crenulated mica by green phyllosilicate was evident in optical microscopy of samples from Sleaford Bay, including replacement of mica interleaved with graphite (Fig. 2). The alteration was associated with chalcedony, cherty quartz and iron oxide. Remnant primary minerals were K-feldspar, garnet, magnetite and possibly pyroxene. Under scanning electron microscopy (SEM) celadonite appeared as masses of thin laths and as layers with cryptomelane ($K(Mn_6^{4+}Mn_2^{3+})O_{16}$) or silica lepispheres, on graphite (Fig. 3). Celadonite was confirmed by XRD, probably 1M polytype, with (060) reflection corresponding to d-spacing of 1.510 Å. Fine-grained goethite present with Sleaford celadonite (Fig. 4a) was effectively removed by sizing and acid treatment, but celadonite from the Uley mine was too kaolinised to determine mineral composition (Fig. 4b). Chemical analysis of Sleaford Bay celadonite gave a composition of ferroceldonite $K_{0.82}Na_{0.03}(Fe^{3+}_{1.08}Al_{0.06}Fe^{2+}_{0.20}Mg_{0.55})Si_4O_{9.9}(OH)_{1.98}(H_2O)_{0.12}$.

Results from K-Ar dating of celadonites were as follows:

- Sleaford Bay 0.2-2 µm 48.9±1.1 Ma; 3-1 µm 46.1±1.0 Ma (early Eocene),
- Uley mine 2-5 µm samples UGCE1 20.9±0.7 Ma; UGCE4 16.7±0.4 Ma; UGCZ 15.4±0.6 Ma (early Miocene).

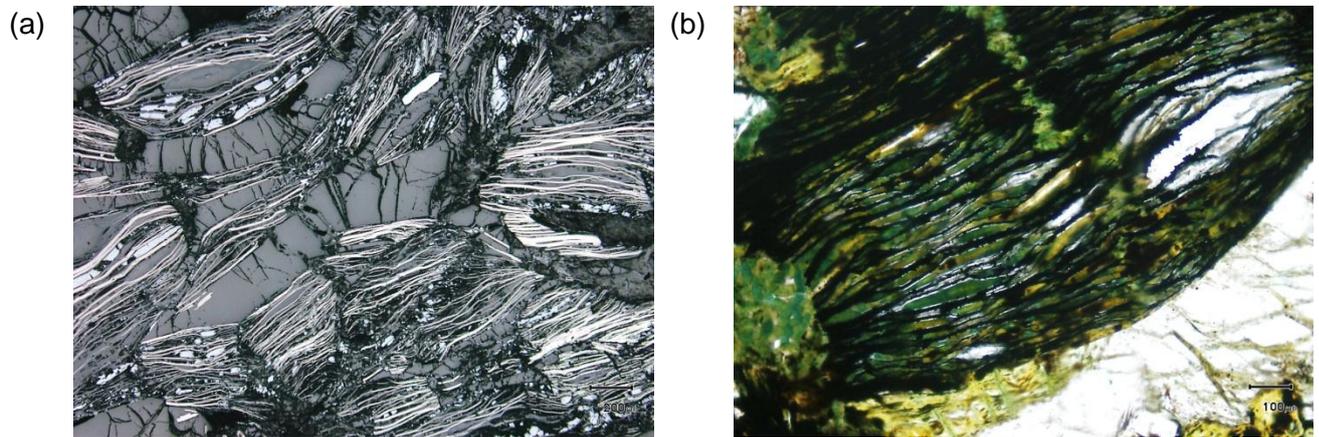


Fig. 2. (a) Reflected light image of polished section showing graphite (white), with interleaved phyllosilicate alteration and coarse K-feldspar, scale bar 200 µm. (b) Detail of celadonite (green) replacing mica, interleaved with graphite (black), and as veinlets, with granular K-feldspar (white) - thin section with crossed nicols, scale bar 100 µm.

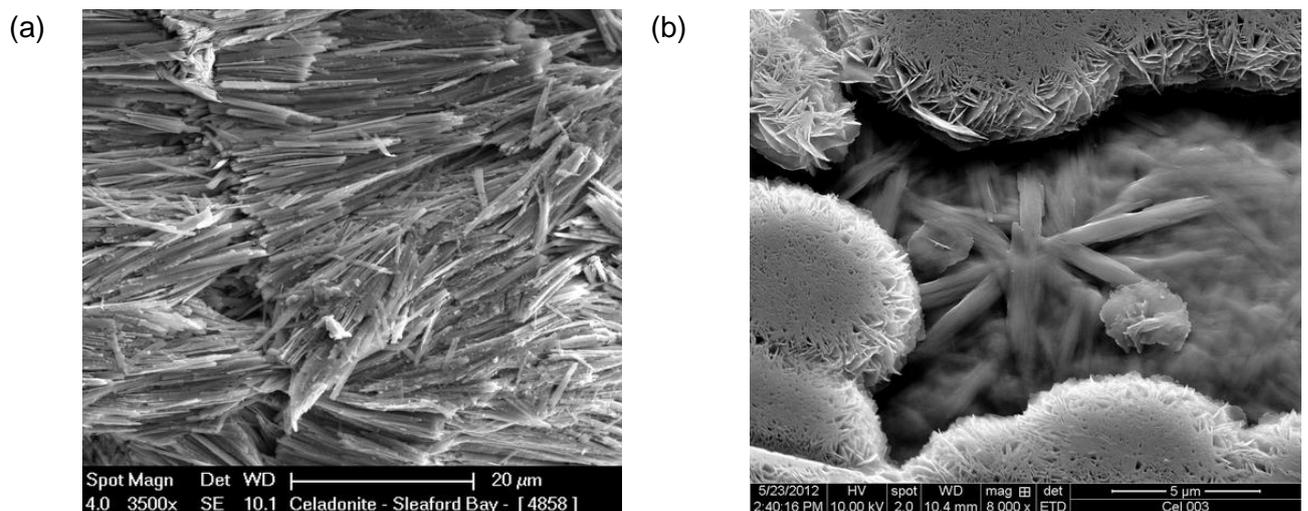


Fig. 3. Sleaford Bay celadonite - SEM secondary electron images (a) Masses of celadonite laths as vein infill (b) Radiating celadonite laths coated by silica lepispheres as alteration products interleaved with flake graphite.

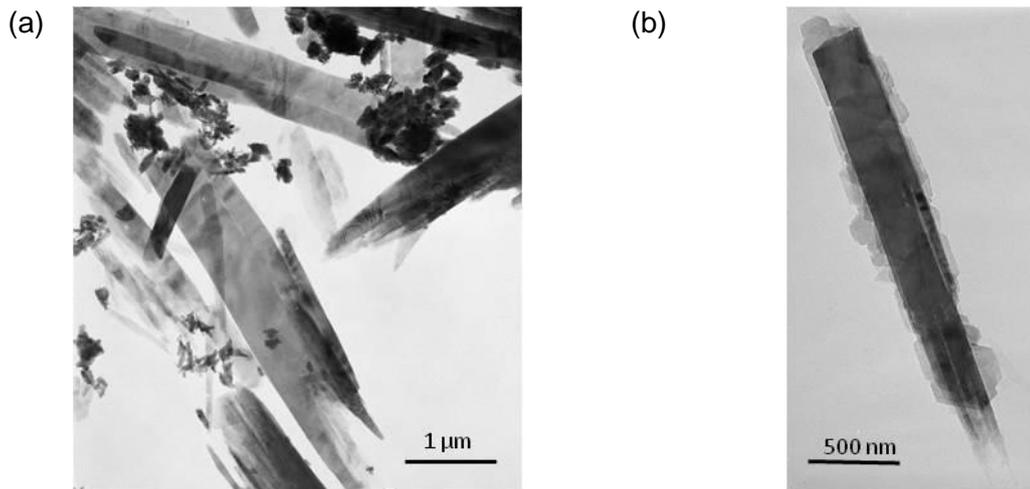


Fig. 4. (a) Transmission electron micrograph: Sleaford Bay - celadonite laths with fine-grained goethite, (b) Uley mine - celadonite lath partly altered to kaolinite (pseudo-hexagonal overgrowths).

Discussion

Celadonite at the Uley mine and Sleaford Bay is the alteration product of mainly biotite in schist and micaceous gneiss of Paleoproterozoic high-grade metamorphic rocks. The timing of alteration, early Eocene and early-mid Miocene, is a strong indication that the alteration is related to Cenozoic deep weathering, widely preserved across southern Australia. The mineralogy, however, is unusual in that biotite typically alters to kaolin and iron oxide in deeply leached profiles, under neutral to acidic conditions. Also, the two main time intervals for celadonite crystallisation correlate with local high sea levels marked by the onset of sedimentation of Wilson Bluff Limestone and Nullabor Limestone respectively, in nearby Eucla Basin. The Sleaford Bay site would most probably have been below sea level during both periods of celadonite formation. An explanation needs to take into account also that on southern Eyre Peninsula, celadonite alteration, with or without nontronite, has so far only been observed at sites of highly graphitic rocks.

Graphitic rocks facilitate shearing and tend to concentrate fracturing during deformation. These often are zones of high permeability that focus fluid flow, resulting in greater depth of weathering and increased flux of meteoric water. Chemical weathering and oxidation creates a spontaneous potential between the weathered zone and fresh rock that induces gradual movement of negatively charge-carrying species towards the zone of oxidation. Graphitic shear zones can act as conductive bodies that focus the flow of negative charge leading to increased consumption of oxidising agents around the upper part of the conductor, resulting in more reduced conditions in the area around the top of the conductor relative to adjacent areas. Once established, the electro-chemical cell could continue to operate when flooded by seawater. Other fluid circulations induced by salinity contrast, or by seismic or thermal activity on the nearby Kalinjala shear zone may also have been in operation. Saline, alkaline, and more reduced oxidising conditions are consistent with the style of alteration incorporating celadonite, nontronite, chalcedonic silica, and cryptomelane.

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