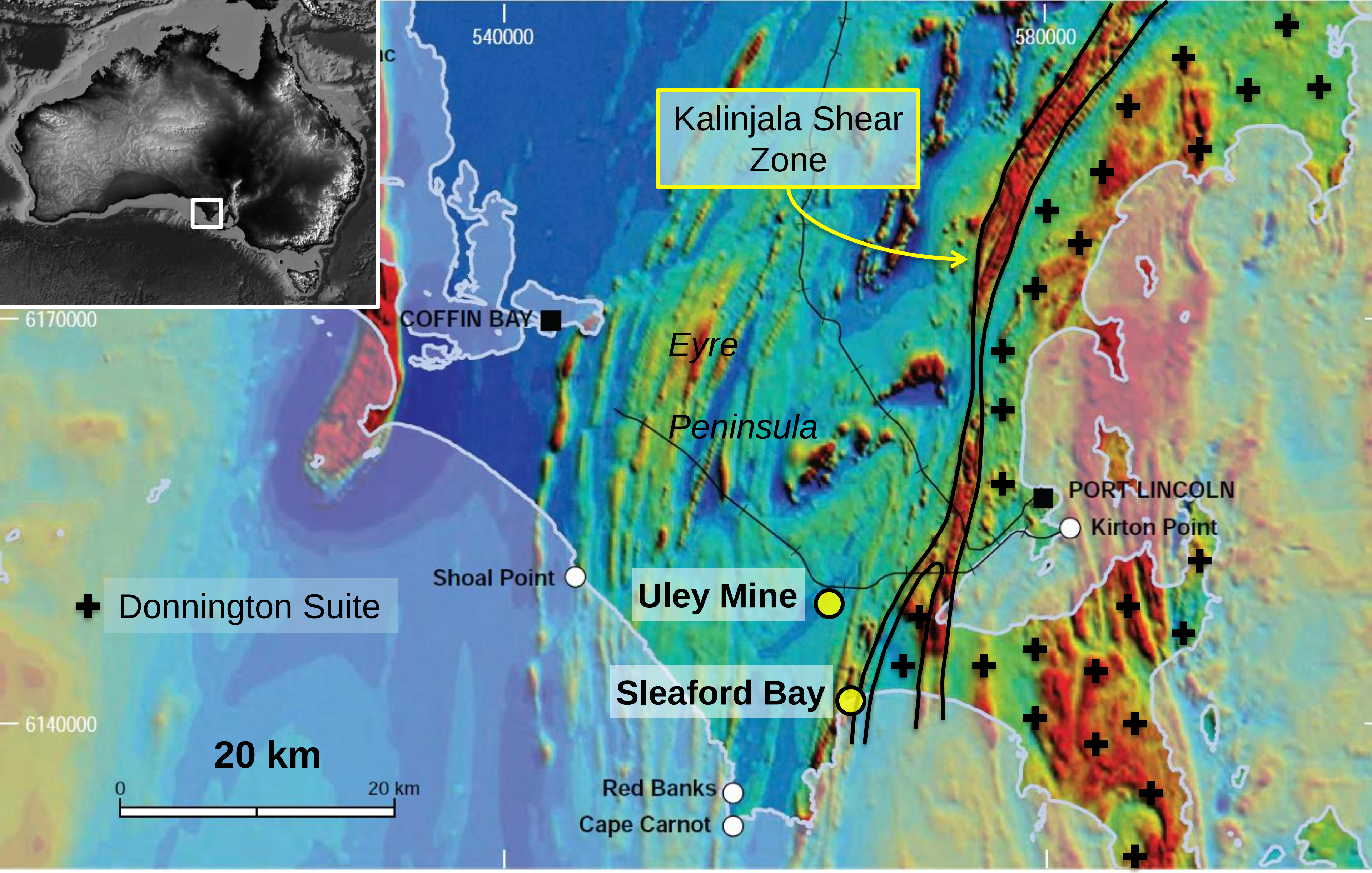
Atypical biotite alteration: timing and environmental factors

Keeling[1], Zwingmann[2], Raven[3] & Self[3]

[1] Geological Survey of South Australia

[2] Kyoto University, Japan

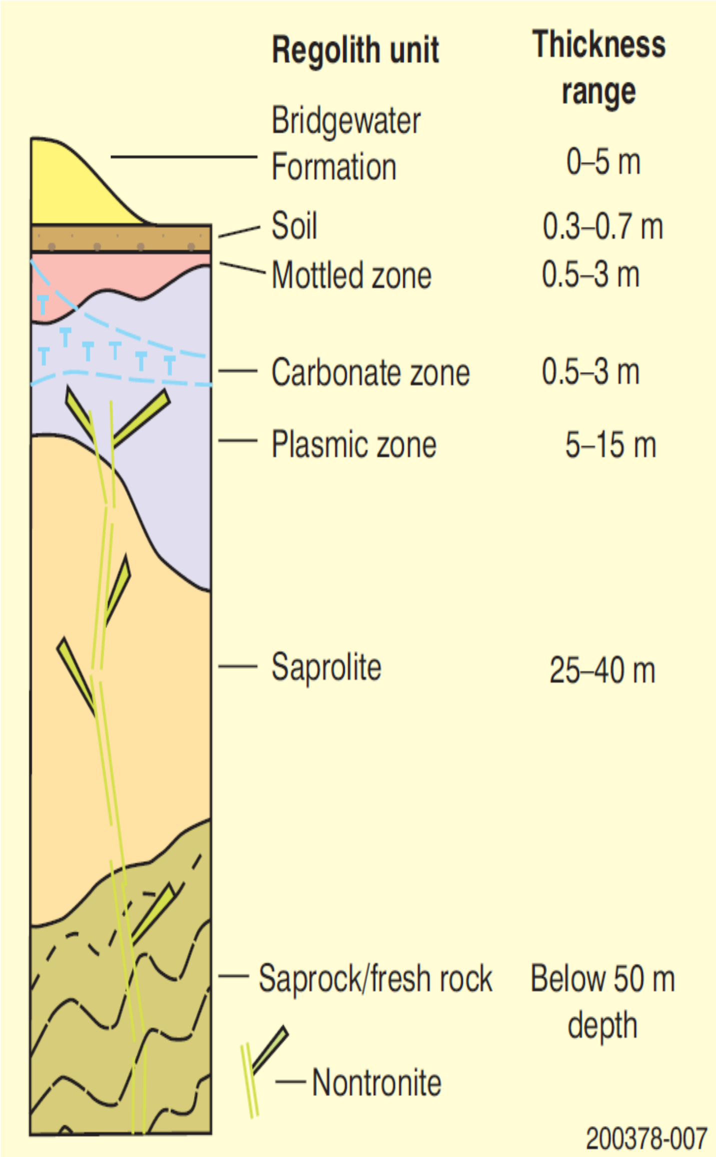
[3] CSIRO Land and Water

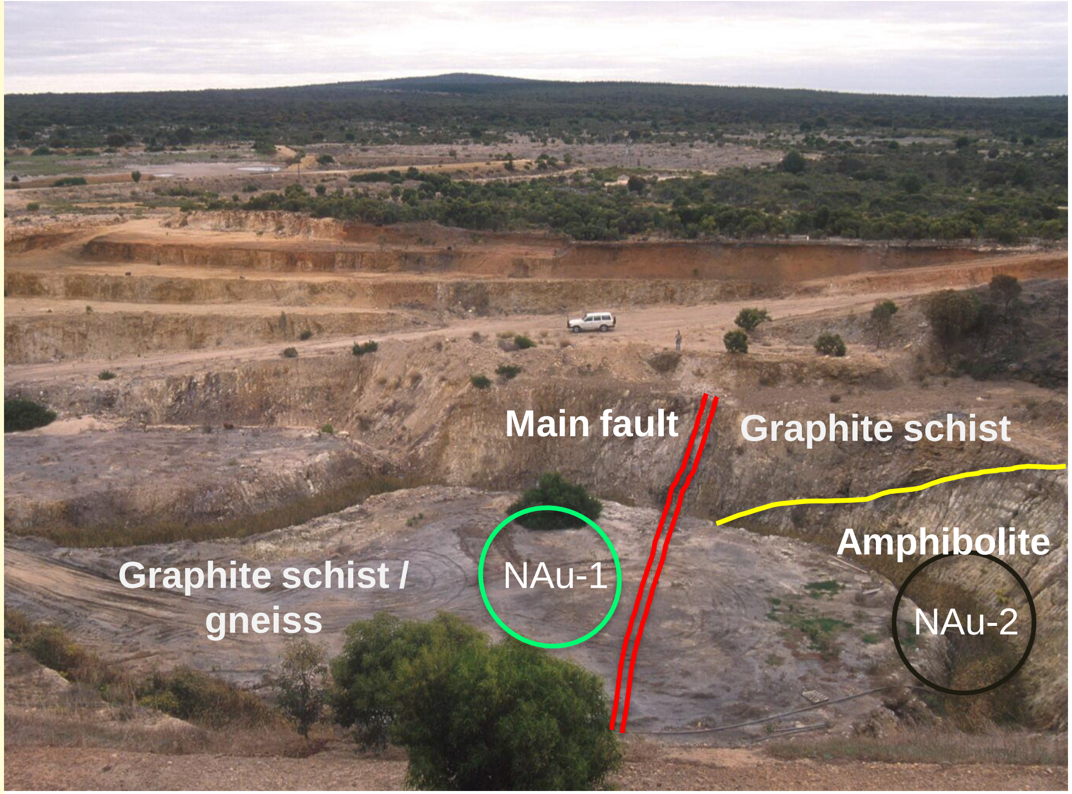


Celadonite sites, southern Eyre Peninsula

(on Total Magnetic Intensity (TMI) image)

Uley Graphite Mine

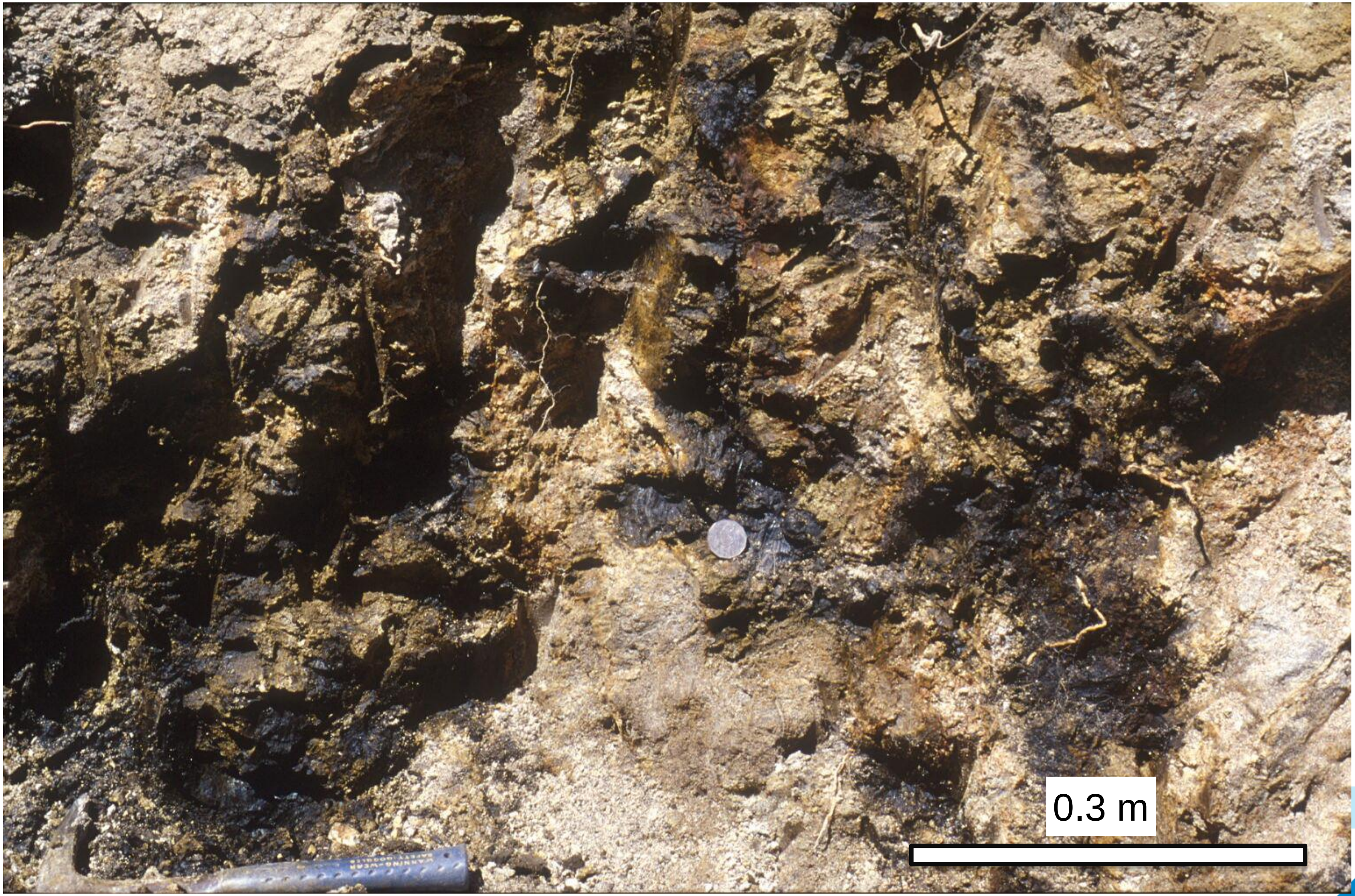




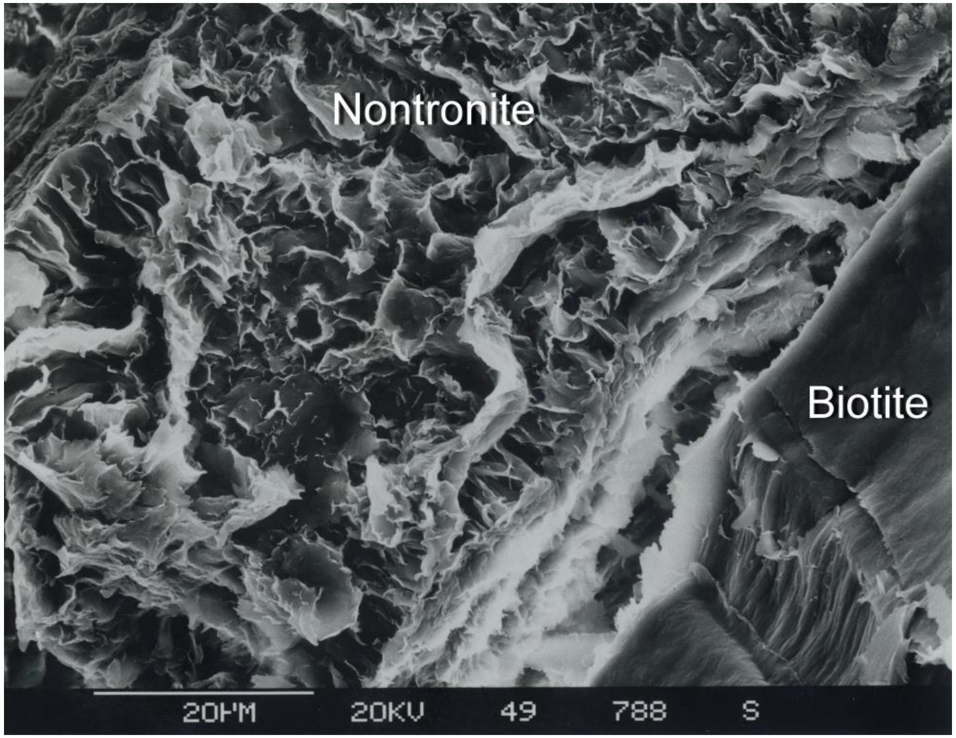
Uley Graphite Mine - view easterly, 1996

Generalised regolith section showing patchy nontronite alteration distributed around fault and fracture zones

Uley brown nontronite: (NAu-2) in altered amphibolite



Uley green nontronite: (NAu-1) nontronite after biotite



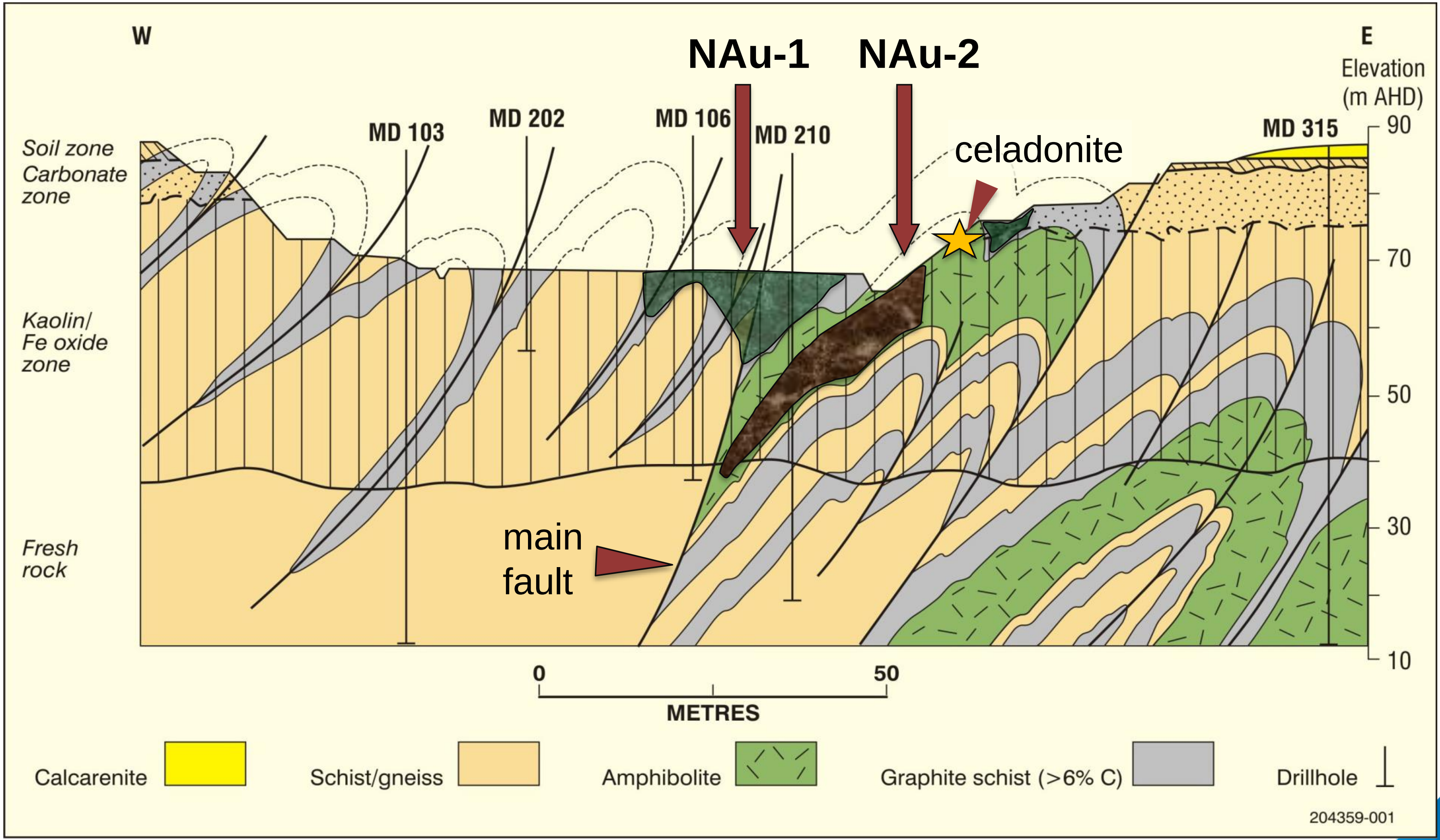
NAu-1 Uley green nontronite - alteration product of biotite in graphite-biotite schist

Uley Graphite Mine 2012 – celadonite

Remnant **celadonite** in kaolinised amphibolite

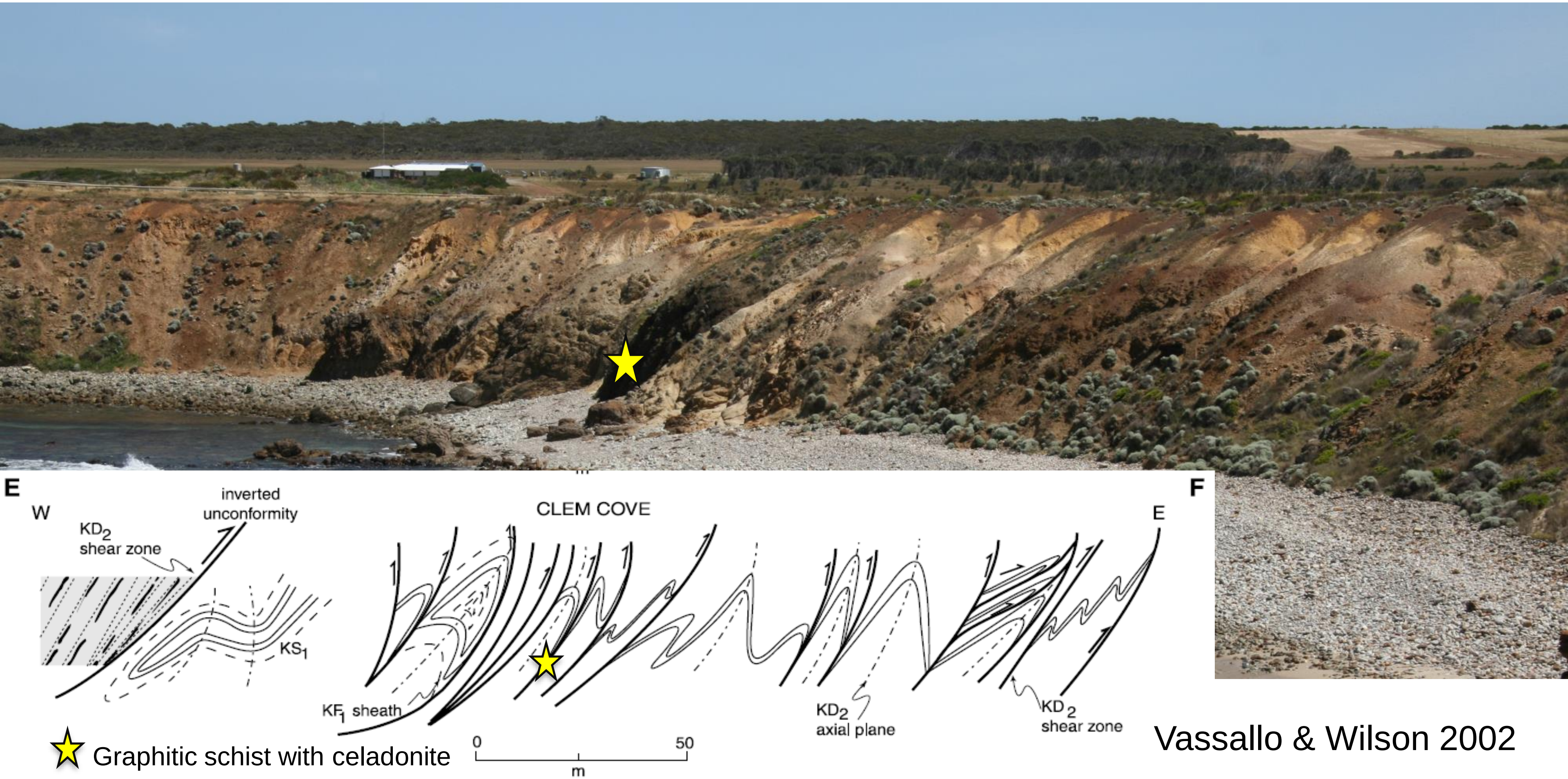
Celadonite: Fe-rich dioctahedral ‘white mica’

Uley Graphite Mine – Geological Section



CMS Nontronite: NAu-1 and NAu-2 – celadonite in plasmic zone

Sleaford Bay – Clem Cove section



Vassallo & Wilson 2002

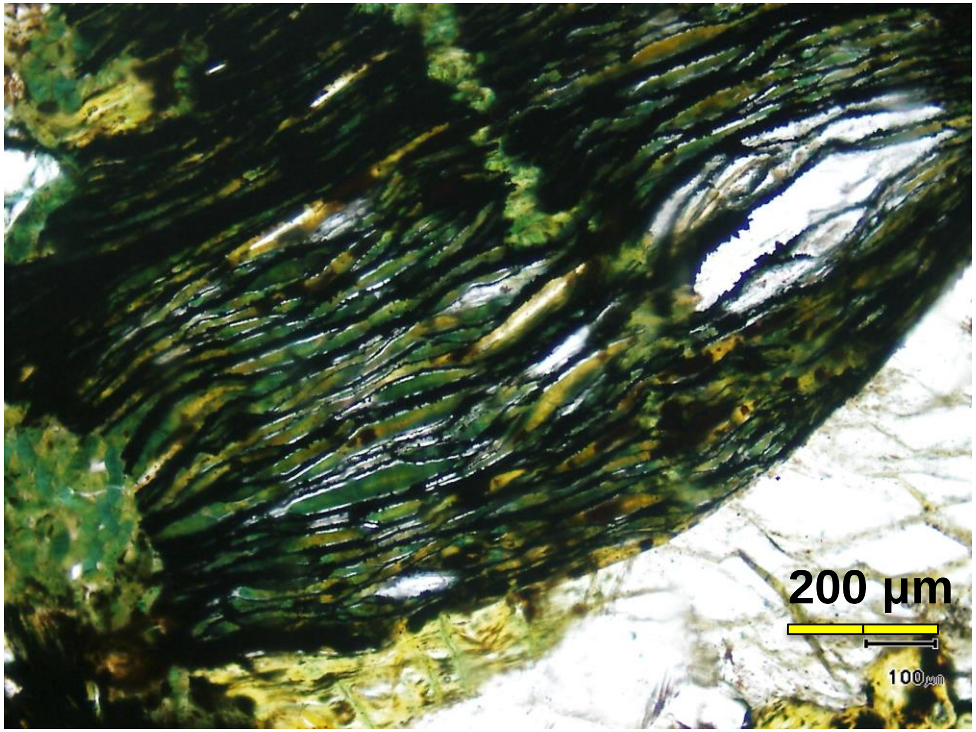
Key outcrop of Paleoproterozoic Hutchison Group with graphitic units.

Section mapped several times from Tilley (1921) to Vassallo and Wilson (2001, 2002) – granulite facies metasediments, highly deformed.

Sleaford Bay - Clem Cove graphitic schist and gneiss

Detail showing celadonite, iron oxide and manganese oxide altered graphite-rich schist

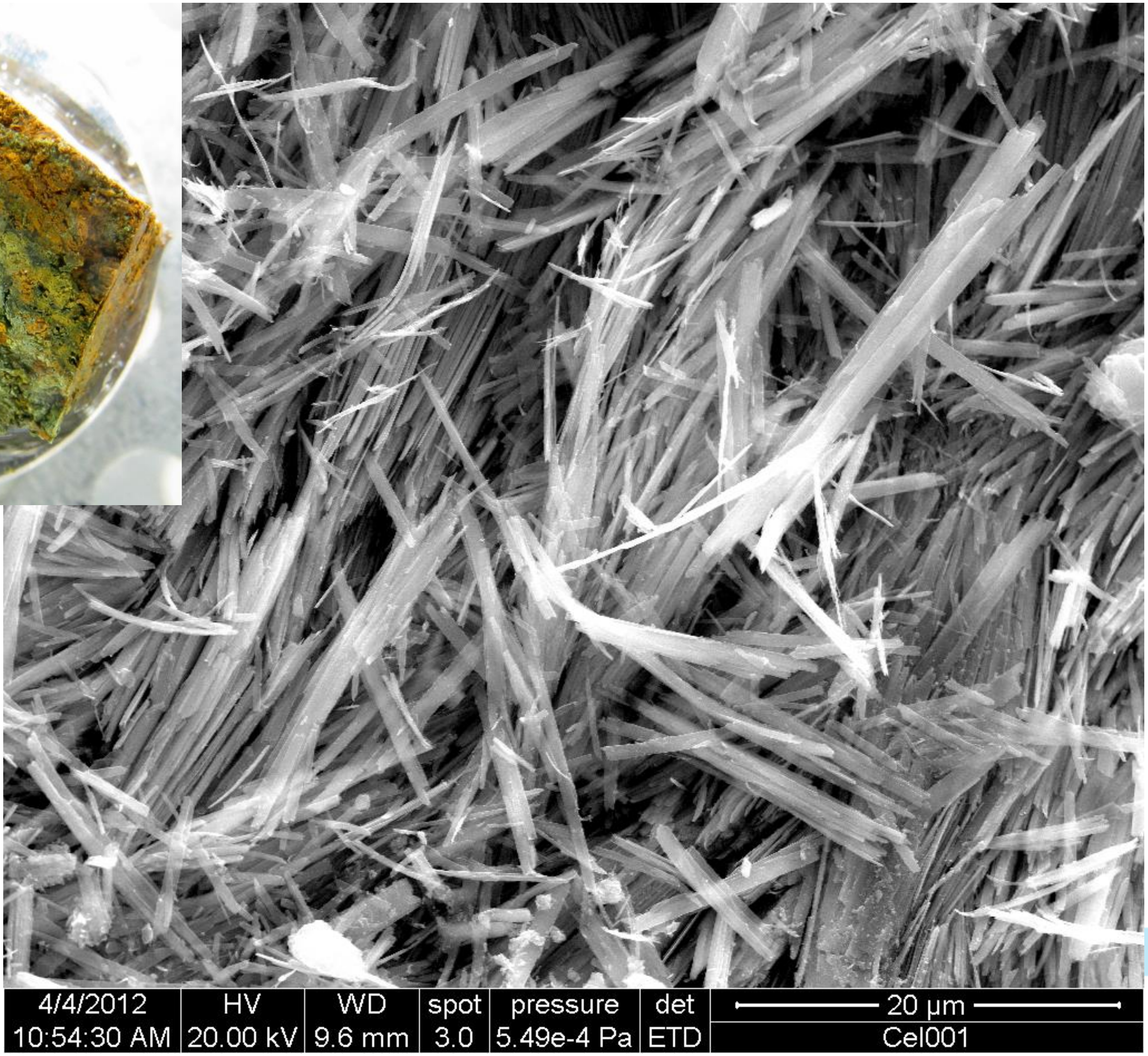
Sleaford Bay celadonite



Highly altered graphite-biotite schist:

Celadonite forms as veins and replacement of biotite interleaved with flake graphite

Sleaford Bay celadonite - SEM



Celadonite as lath-shaped fibre masses as fracture infill and replacement of biotite interleaved with graphite

Celadonite: conditions for formation

- Nontronite and celadonite form precipitates in basalt, at sites of active sea-floor spreading. Sub-oxic conditions and temperatures up to 90°C.
- Submarine ‘weathering’: saponite, celadonite, nontronite form by alteration of volcanic glass in basalt by slow circulating seawater. Largely an oxidation process, high Fe^{3+} content in celadonite and nontronite, but buffered by reactions to slightly reducing (Velde 2003). Alteration fluid temperatures <30°C.
- “Continental meteoric fluids generally too oxidizing and have too low a cation content to favour the genesis of celadonite.” (Odin et al. 1988).
- Keeling et al. (2000) concluded that at Uley graphite mine, nontronite and celadonite formed by low temperature hydrothermal activity, later overprinted by deep weathering.
- Celadonite was recently described from continental flood basalts - O_2 fugacity and fluid composition buffered by basalt groundmass dissolution and celadonite crystallisation (Baker et al. 2012).

Biotite alteration

- Weathering
  - Biotite → biotite interstratified with vermiculite or smectite
    - → vermiculite or smectite (montmorillonite – neutral/alkaline pH)
      - → kaolinite or halloysite and amorphous Fe^{3+} (hydr)oxide (which converts to goethite (α-$Fe^{3+}OOH$)).
- Hydrothermal (low temperature)
  - Biotite → chlorite, phengitic 'white mica', illite, or halloysite / kaolinite
- While biotite alteration to Fe-rich smectite (nontronite) is uncommon but feasible, biotite weathering to celadonite is highly unusual.

Celadonite – K-Ar dating results

Site	Sample	K (%)	Age Ma	Error Ma	δO^{18} per mill
Sleaford Bay	0.2-2 µm	6.69	**48.9**	1.1	21.9
	3-1 µm	6.94	**46.1**	1.0	21.8
Uley Mine	UGCE1	3.34	**20.9**	0.7	21.8
	UGCE4	3.68	**16.7**	0.4	21.3
	UGCZ 2-5 µm	3.25	**15.4**	0.6	21.8

Timing of celadonite formation – origin?

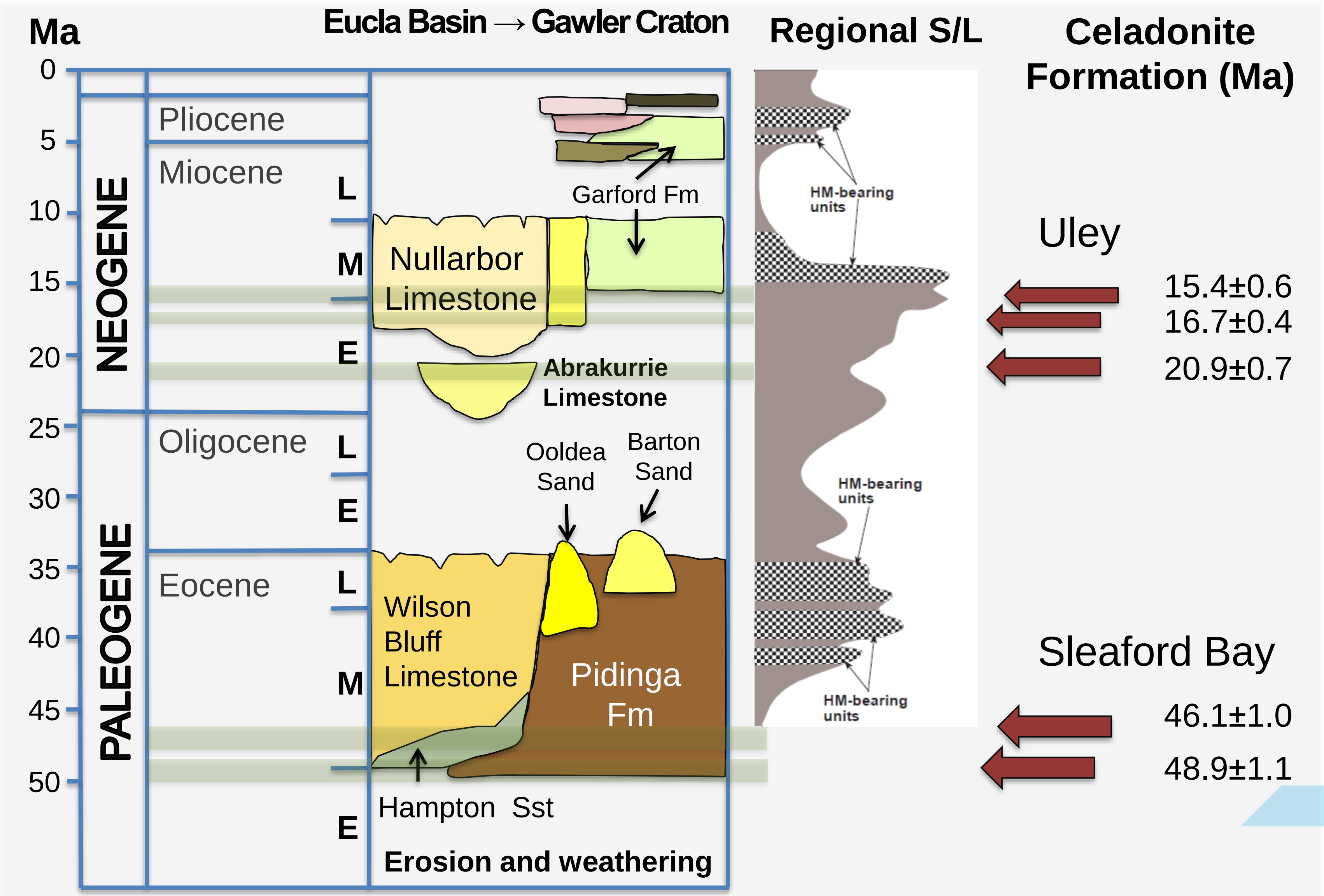
- Celadonite formation during the Cenozoic is more likely a product of weathering – no igneous or hydrothermal activity recorded in the region at this time.

- Oxygen isotope results of ~21.8‰ are consistent with lowest temperatures estimated for oceanic basalt alteration (<30°C) (Odin 1988).

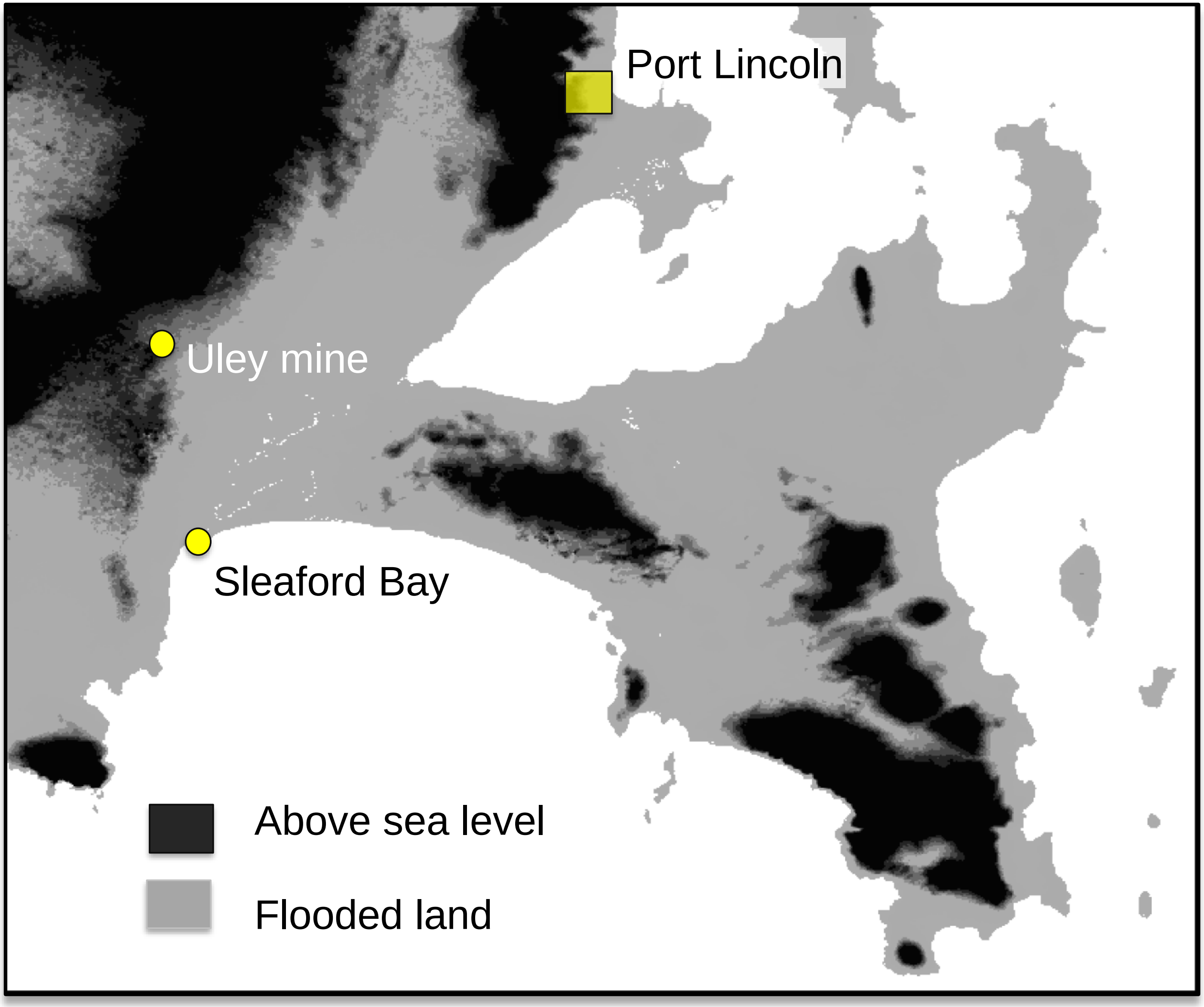
- Why then celadonite and nontronite after biotite rather than vermiculite / montmorillonite – kaolin – goethite?

- Local environmental factors and the presence of graphite?

Celadonite formation - timing and sea level change



Southern Eyre Peninsula – flooded to 90 m (Miocene s/l?)

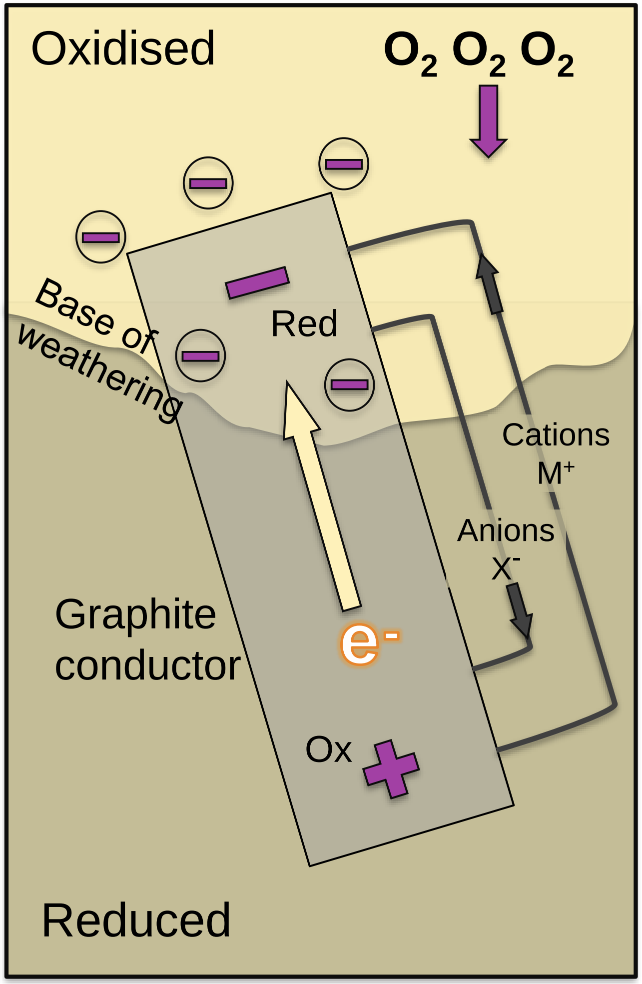


Possibility that the weathering reactions at these sites were buffered by groundwater with sea-water salinity

Neutral to alkaline pH

Effect of weathering around graphitic conductors

Natural voltaic cell



- Redox reactions require electron transfer

  (e.g. $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$)

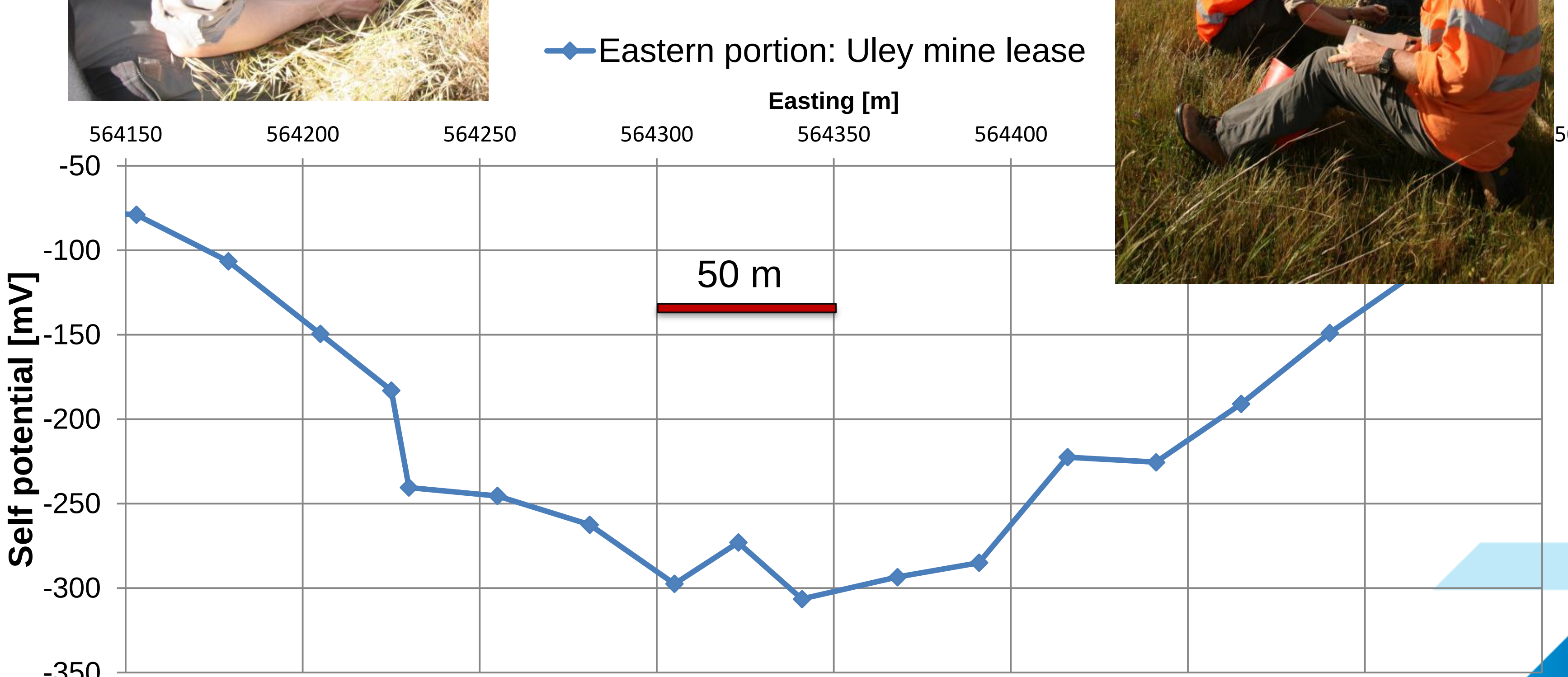
  One source: $4Fe^{2+} \rightarrow 4Fe^{3+} + 4e^-$

- Weathering / oxidation gives rise to a potential difference between the oxidised and reduced zones

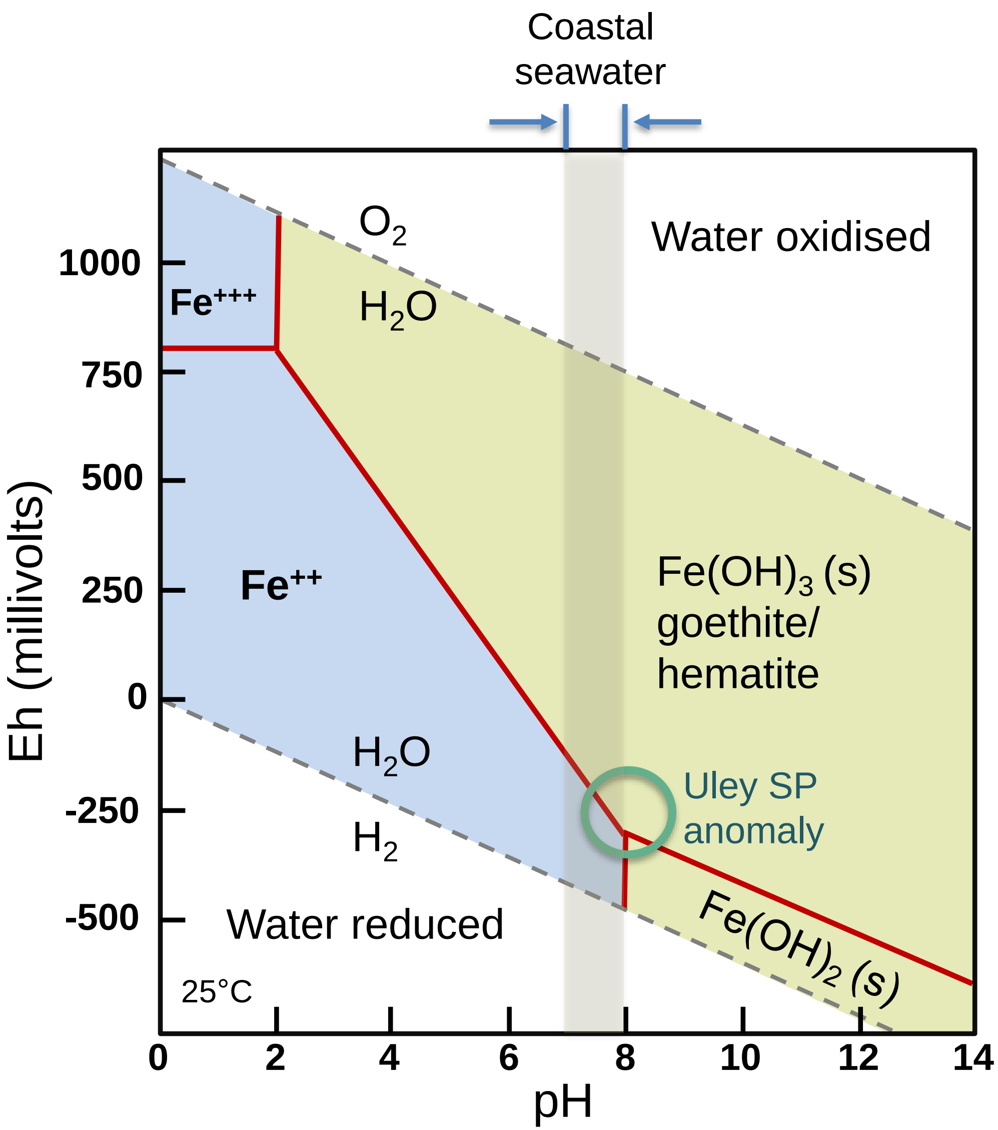
- Conductive bodies (e.g. graphite) facilitate the flow of negative charge (electrons/ions) - gives rise to natural spontaneous potential (SP) negative anomaly – with a relatively reduced environment around the upper zone of the conductor (Sato & Mooney 1980)

SP Survey Uley Mine - 2012

Self Potential (SP) anomaly over Uley Graphite orebody -100 mV to -300 mV



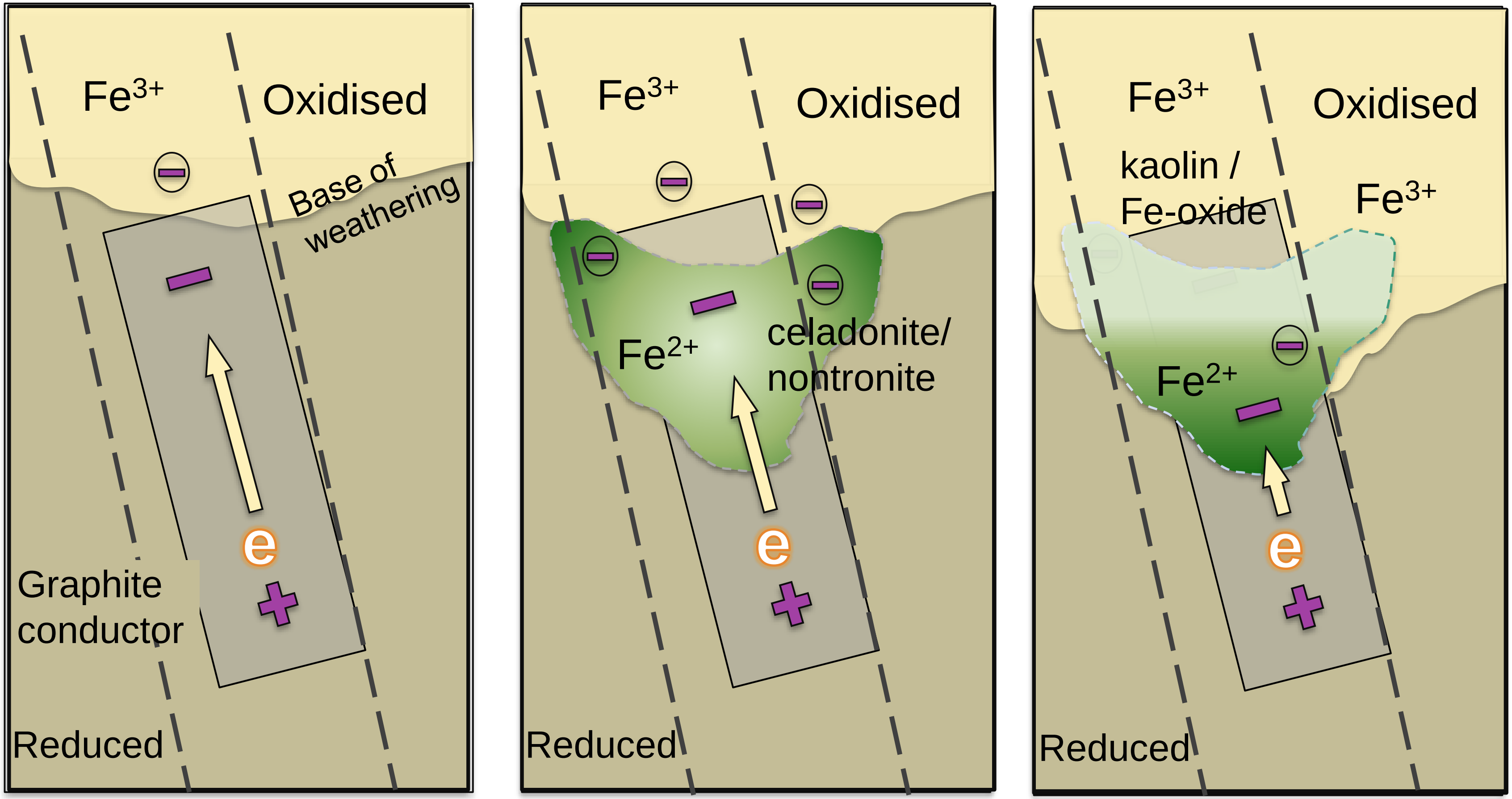
Eh-pH stability fields for Fe in water at 25°C



- Self Potential (SP) anomaly of -100 mV to -300 mV at the Uley graphite mine indicates localised areas of reduced groundwater, sufficient to permit Fe^{2+} to remain in solution at neutral to slightly alkaline pH of 7-8 (e.g. seawater buffer).
- Conditions suitable for crystallisation of nontronite and celadonite

(Simplified Eh-pH diagram for Fe modified from Dill et al. 2010)

Alteration during bedrock weathering modified by graphite conductor



Summary

- Biotite alteration to nontronite and celadonite is not typical.
- Nontronite / celadonite are characteristic of low temperature hydrothermal alteration of oceanic basalt.
- Requires a neutral to slightly alkaline, oxidising to reducing environment (i.e. maintain high activity of Fe^{2+} and Fe^{3+} ions).
- These conditions might be replicated for Fe-rich mineral alteration around a conductive graphite body in saline groundwater, due to anomalous electro-chemical activity that develops in response to weathering.
- Possible implications for the role of graphite in low temperature redox reactions leading to precipitation of uranium from groundwater – with particular relevance to unconformity-related uranium deposits.

References

Baker LL, Rember WC, Sprenke KF, Strawn DG 2012. Celadonite in continental flood basalts of the Columbia River Basalt Group. American Mineralogist 97: 1284-1290.

Cervini-Silva J, Palacios E, Gómez-Vidales V (in press, 2018). Nontronite as natural source and growth template for (nano)maghemite [y-Fe_2O_3] and (nano)wüstite [$Fe_{1-x}O$]. Applied Clay Science.

Dill HG, Hansen B, Keck E, Weber B 2010. Cryptomelane: A tool to determine the age and the physical-chemical regime of a Plio-Pleistocene weathering zone in a granitic terrain (Hagendorf, SE Germany). Geomorphology 121: 370-377.

Keeling JL, Raven MD, Gates WP 2000. Geology and characterization of two hydrothermal nontronites from weathered metamorphic rocks at the Uley graphite mine, South Australia. Clays and Clay Minerals 48: 537-548.

Odin GS, Desprairies A, Fullagar PD, Bellon H, Decarreau A, Frohlich F, Zelvelder M 1988. Nature and geological significance of celadonite. In: Odin GS (ed.) Green marine clays, Developments in Sedimentology 45: 337–398, Elsevier, Amsterdam.

Velde B 2003. Green clay minerals. In: MacKenzie FT (ed.) Sediments, Diagenesis, and Sedimentary Rocks p. 309–324, Pergamon, Oxford.