# Spatiotemporal $\Delta^{17}O$ variability in the rock record

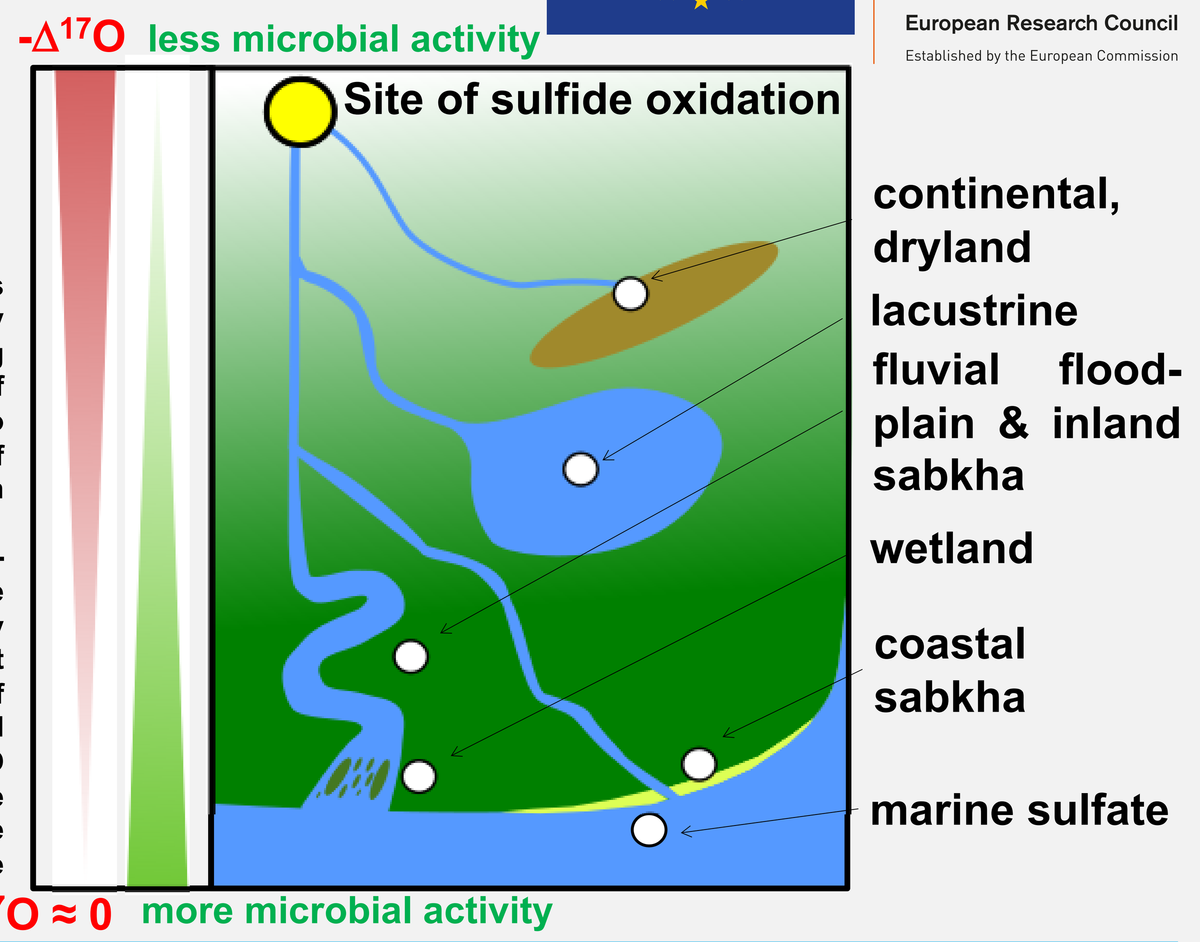
Matthew R. Warke[1], Ross P. Pettigrew[2], David Millward[3], Robert J. Raine[4], Charlotte Priddy[2], Stuart M. Clarke[2], Yongbo Peng[5], Huiming Bao[5], Eva E. Stüeken[1] and Mark W. Claire[1]

**Rationale.** Negative $\Delta^{17}O$ signal in sedimentary sulfate inherited from atmospheric $O_2$ during atmospheric weathering and transported via surface run-off/fluvial systems to depositional environments and, ultimately the marine sulfate reservoir. Sulfate oxygen is non-labile, but can be exchanged by microbial activity making $\Delta^{17}O$ conservative tracer of interplay between $pCO_2$, $pO_2$, and primary productivity.

**Hypotheses.** Microbial recycling of sedimentary sulfate and erasure of the negative $\Delta^{17}O$ signal becomes more pronounced downstream away from source of weathering (Fig. 1). This leads to spatial variability in $\Delta^{17}O$ at any given time. Despite potential complications, this could be a first-order control on $\Delta^{17}O$ in geological record. We make two predictions which we test in two case studies:

- **CASE-STUDY 1:** Non-marine environments will preserve the most negative $\Delta^{17}O$ signal at a given time.
- **CASE-STUDY 2:** Progressively marine-influenced environments will see a coupled $\Delta^{17}O$-$\delta^{34}S$ trends reflecting a transition from fluvial to marine dominated signals.

Fig. 1: how $\Delta^{17}O$ values might progressively increase with increasing distance from the site of sulfide oxidation due to higher levels of microbial activity in downstream environments. Environments closer to the site of sulfide oxidation may preserve the most negative $\Delta^{17}O$ values of any given time period and marine sulfate $\Delta^{17}O$ values might be the most conservative values at any given time period.




## CASE-STUDY 1: early Permian Cedar Mesa Sandstone Formation (Utah, USA)*

***all figures from:** Pettigrew, R.P, Priddy, C., Clarke, S.M., Warke, M.R., Stüeken, E.E., and Claire, M.W. *submitted*. Sedimentology and Isotope Geochemistry of Transitional Evaporitic Environments within Arid Continental Settings: From Erg to Saline Lakes. *Sedimentology.*

### Background

- Cedar Mesa Sandstone (CSM) deposited in Carboniferous Paradox Basin, SE Utah during the early Permian.
- Consists of sandstone with minor mudstone, siltstone, evaporites (gypsum) and carbonates.
- Originally considered aeolian (pre-1950) and revised to shallow marine (1960-1980), but now consensus indicates it is aeolian and non-marine (1980-onward) but small $\delta^{34}S$ dataset overlaps with marine curve[1].

### Goals

- Coupled sedimentological and isotopic study of CSM.
- Determine depositional settings and processes.
- Assess field and petrographic evidence for non-marine vs marine influence on succession and evaporites.
- New, well-constrained O and S isotope dataset.

### Methods

- 10 sedimentological logs measured through CSM and optical petrography of hand samples conducted.
- Log 1.4 (Fig. 2) selected for high resolution XRD, $\Delta^{17}O$, $\delta^{18}O$ and $\delta^{34}S$ analysis.

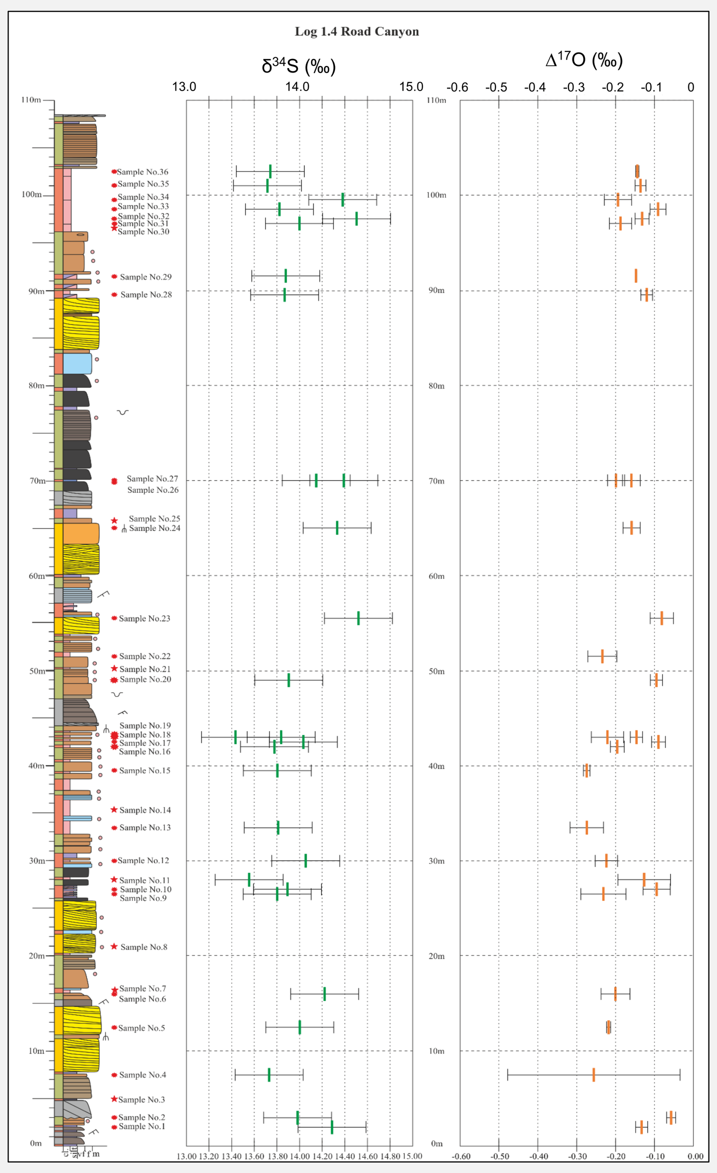



Fig. 2: $\delta^{34}S$ and $\Delta^{17}O$ values from Log 1.4.

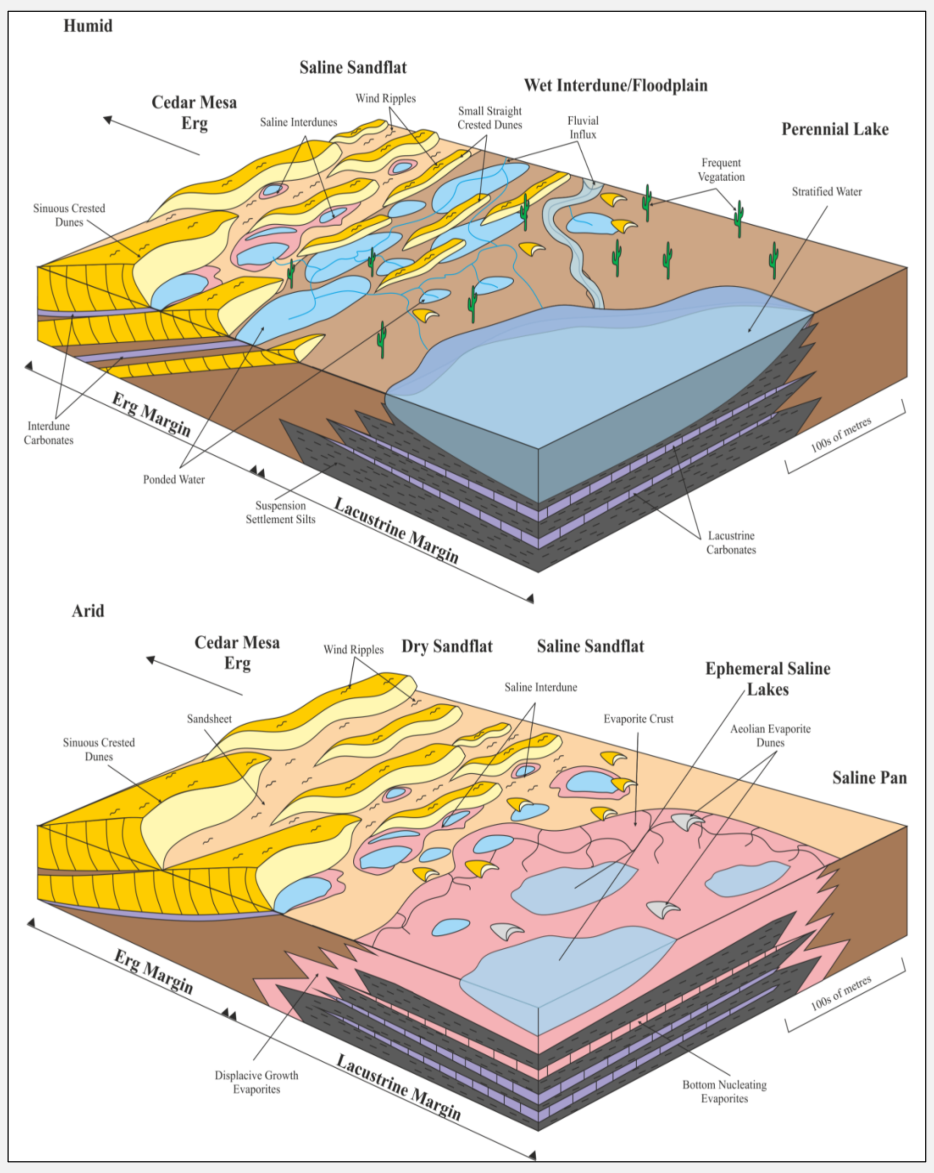



Fig. 3: spatial distribution of depositional settings in each climatic (arid/humid) regime.

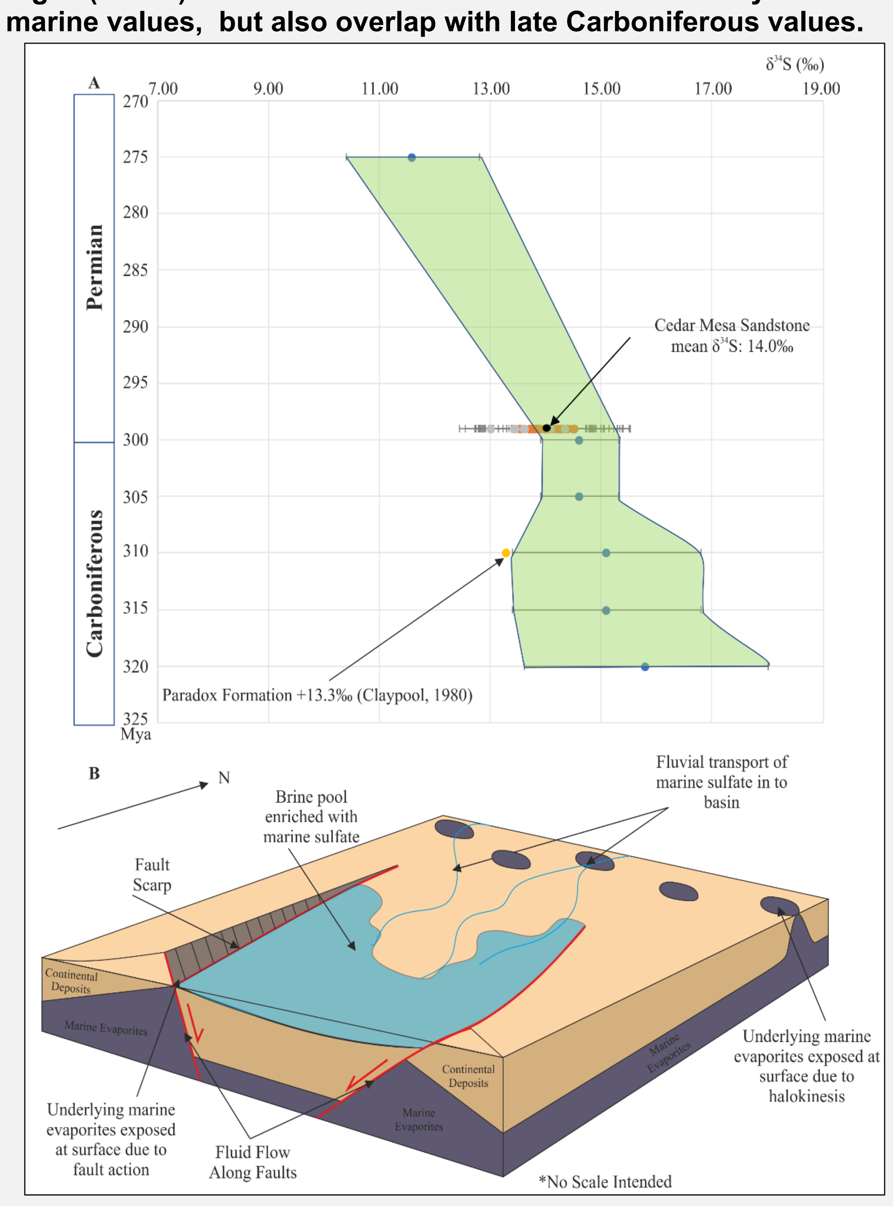
### Discussion

- Facies associations suggest several environments (Fig. 3) spanning the interface between erg and lacustrine settings. Cyclicity was driven alternating climatic regime (humid vs arid).
- No evidence suggesting marine influence on sedimentation.
- Propose that 'marine' $\delta^{34}S$ is sourced from continental weathering of underlying late C marine evaporites of Paradox Formation (Fig. 4).
- Sulfate complex is decoupled from age of succession. <u>Sulfate recycling in non-marine, continental settings holds important implications for temporal compilations of $\Delta^{17}O$ used to constrain atmospheric evolution</u>.

### Results

- 15 lithofacies deposited in sub-aerial, subaqueous, and evaporitic settings and group into nine facies associations.
- Bedded (primary), displacive (early diagenetic) and brecciated gypsum facies observed.
- Gypsum all facies: $\delta^{34}S$ = +13.4 to +14.5 ±0.3 ‰ and $\Delta^{17}O$ = -0.27 to -0.06 ± 0.05 ‰ (Fig. 2). Most negative $\Delta^{17}O$ measured from this time period.

Fig. 4 (below): CSM $\delta^{34}S$ values fall within or below early Permian marine values, but also overlap with late Carboniferous values.




## CASE-STUDY 2: early Carboniferous (Tournaisian) Ballycultra, Ballagan, Middleton Dale Anhydrite formations (UK)

### Background

- Three formations constrained to Tournaisian and span depositional space:
  - **Ballagan Formation[2]** – fluvial floodplain to wetland settings.
  - **Ballycultra Formation[3]** – coastal sabkha on edge of restricted basin.
  - **Middleton Dale Anhydrite Formation[4]** - coastal sabkha on edge of open basin.
- Nodular, chicken-wire and enterolithic gypsum (early diagenetic) fabrics sampled.
- Depositional timeframe spans contentious gap – 'Romer's gap' – in the fossil record of terrestrial tetrapods, speculated to link to low $pO_2$.

### Goals

- Is there significant systematic, spatial, $\Delta^{17}O$-$\delta^{34}S$ variation across depositional environments? Can this be adequately distinguished from temporal variability?

### Methods.

- Samples for XRD, $\Delta^{17}O$, $\delta^{18}O$ and $\delta^{34}S$ analysis gathered from well described drill-cores (Belfast Harbour, Norham, and Eyam).

### Preliminary results and discussion

- Covariation in $\Delta^{17}O$-$\delta^{34}S$ (Fig 5.) could suggest spatial control, but three low $\Delta^{17}O$ Ballagan and two near zero $\Delta^{17}O$ Ballycultra values do not follow relationship. If these (n=6) excluded R = 0.7.
- ~10 ‰ swing in $\delta^{34}S$ over Tournaisian means separating spatial and temporal variability difficult.
- Ballycultra and Middleton Dale show relationships expected (Fig. 1) but why is Ballagan 'more marine'? Is this spatial or is it slightly older than others?
- <u>Most negative $\Delta^{17}O$ measured in Phanerozoic.</u>

### Ongoing work

- $\delta^{18}O$ values to be determined.
- Exploring reason(s) for low $\Delta^{17}O$ in Ballagan Fm. and apparent decoupling from $\delta^{34}S$.
- Coupling of $\Delta^{17}O$ with photochemical modelling to explore atmospheric constraints.

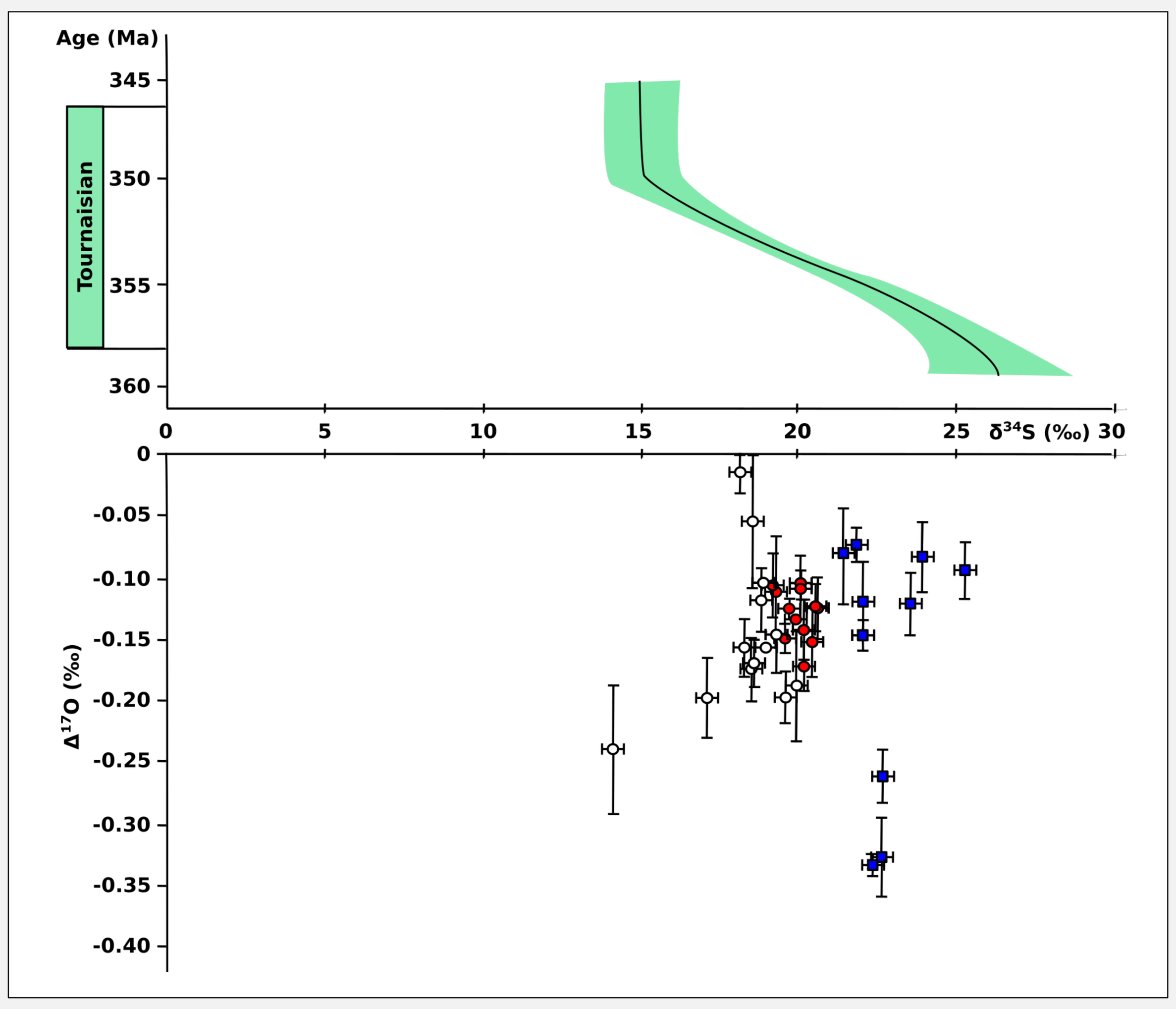



Fig. 5: $\Delta^{17}O$ and $\delta^{34}S$ from the Ballycultra (white circle), Middleton Dale (red circle), and Ballagan (blue square) formations. All values consistent with (early or late) Tournaisian marine evaporite $\delta^{34}S$ values (upper panel).

### Overall conclusions

- **Most negative Phanerozoic $\Delta^{17}O$ values yet measured (both case-studies: Carboniferous-Permian).**
- In non-marine, dryland settings evaporite weathering/recycling may obscure temporal $\Delta^{17}O$ variation.
- Coupled $\Delta^{17}O$-$\delta^{34}S$ across depositional space may indicate predicted spatial variability in $\Delta^{17}O$ preservation.

**Affiliations.** (1) School of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK, (2) Basin Dynamics Research Group, Keele University, Keele, UK, (3) British Geological Survey, The Lyell Centre, Edinburgh, UK, (4) Geological Survey of Northern Ireland, Belfast, UK, (5) Department of Geology and Geophysics, Louisiana State University, Baton Rouge, USA

**References.** (1) Stanesco and Campbell, 1989. *US Geological Survey Bulletin*, **1808**, Chapter F; (2) Millward et al., 2018. *Sedimentology*, **65**, 2278-2311; (3) Smith, 1986. *Report of the British Geological Survey*, **18/6**, 1-13; (4) Strank, 1985. *Geological Journal*, **20**, 227-237