

# Use of strontium isotope ratios and rare earth elements in apatite microphenocrysts for characterization and correlation of Silurian metabentonites: a Scandinavian case study

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The Sr isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) was determined for 10 samples of apatite microphenocrysts separated from Telychian (Silurian) metabentonites from the Garntangen Member, Vik Formation, Oslo, Norway, and two samples from the Lower Visby Formation, Gotland, Sweden. The results for the Norwegian group show a bimodal distribution: a 'low' group (0.7041–0.7043) and a 'high' group (0.7061–0.7065). These groups correspond to the 'primitive' and 'evolved' associations, respectively, as defined by previous work on these same samples based on REE and trace element distribution in bulk rock and apatite. The two Swedish samples gave values of 0.70413 and 0.70638, values that correspond to the two geochemical divisions in Norway. In conjunction with previously published REE and other trace element data for apatite, these data suggest a direct comparison between the Telychian metabentonites of Norway and Sweden. The application of Sr isotope ratios in apatite lends additional support to the conclusion that one pair of Telychian metabentonites from Gotland and Norway represent the same fall-out event. Using the biostratigraphic control of Gotland, which is more robust than that of Garntangen, it is proposed that the Lower Visby Formation in Gotland and the Garntangen Member, Vik Formation in Norway can both be assigned to the *M. spiralis* Biozone.

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## Introduction

Correlation of geographically separate rock sequences is crucial for large-scale geological modelling such as that used for plate tectonic reconstruction. Bentonites, which are pale-coloured clay alteration products of Plinian-type volcanic eruptions, are useful for wide-scale correlation, as their source eruptions are short-lived, possibly only of a few weeks' duration, resulting in a deposit that is laterally extensive, crossing facies boundaries, and providing superb time horizons. Such deposits have the potential to correlate among faunal provinces, unfossiliferous sequences and marine- and land-based volcanic provinces. It is with the first of these three options that this paper is concerned, specifically the assignment of shelf fauna to graptolite zones.

In order to correlate, it is essential to fingerprint either individual horizons or stratigraphic sequences. In metabentonites, which have suffered further alteration since bentonite formation, the composition of the whole rock can only provide limited scope for correlation, based on concentrations of the traditionally 'immobile' elements. Although this approach has been used in some studies (e.g. Kolata et al. 1987), a more promising approach is to separate out resistant heavy minerals such as apatite and use their chemical and isotope signature to characterize the deposit or sequence.

This paper reports the first Sr isotope data on European metabentonites, focusing on the Telychian stage, which is the uppermost stage of the Llandovery, at a time when the tectonic plates of Baltica, Avalonia and Laurentia were converging and generating widespread volcanic activity (Batchelor & Clarkson 1993; Batchelor & Jeppsson 1994;



Fig. 1. Sketch map of southern Scandinavia showing the locations of the study areas. Details of the Hønefoss area (Norway) are provided in Batchelor et al. (1995) and of the Lusklint area (Gotland) in Batchelor & Jeppsson (1994).

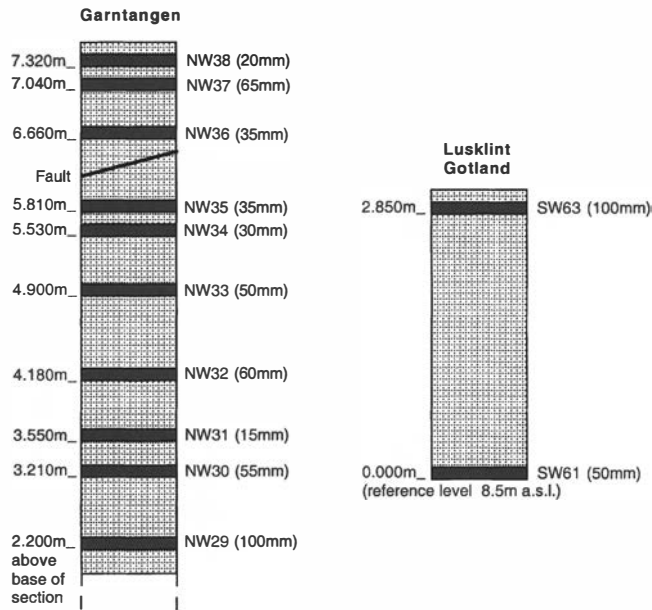


Fig. 2. Schematic stratigraphical log of Telychian metabentonites at Garntangen and Lusklint localities. NW and SW numbers relate to samples analysed in this study. Stippled pattern – limestone/mudstone; black – metabentonite.

Batchelor et al. 1995; Batchelor 1995; Fortey et al. 1996). The extensive occurrence of metabentonites in these sedimentary sequences coincided with a period when graptolite evolution was at its most rapid (Loydell 1993). The graptolites of the Silurian give the greatest biostratigraphical resolution, potentially in the order of 0.1–0.2 Ma (Cope 1993). However, although the high-resolution subdivisions are feasible, the existence of barren beds, provincialism, and the need for taxonomic revision currently frustrate international and intercontinental correlation.

In this study we assess the potential for the use of Silurian metabentonites from Scandinavia as absolute time planes to aid correlation between localities and faunal provinces. Two locations of Telychian age are targeted in this study: the Lower Visby Formation of Gotland, Sweden and the Garntangen beds of Norway (Fig. 1).

Summary of lithology and palaeontology

The Lower Visby Formation is a sequence of marls and limestones with a distinctive fauna of conodonts, representative of the upper *Pterospiriferus amorphognathoides* zone and the rugose coral *Palaeocyclus porpita*. Such an assemblage is typical of a shelf environment, and the preservation of the metabentonites within the sequence indicates formation below wave base in >70 m of water (Grey et al. 1974). In terms of correlation with graptolite zones, the fauna of this sequence correlates with part of graptolite Biozone *M. spiralis* (Aldridge et al. 1993). The Garntangen sequence is another shelf sequence comprising predominantly nodular limestone. It covers the transition

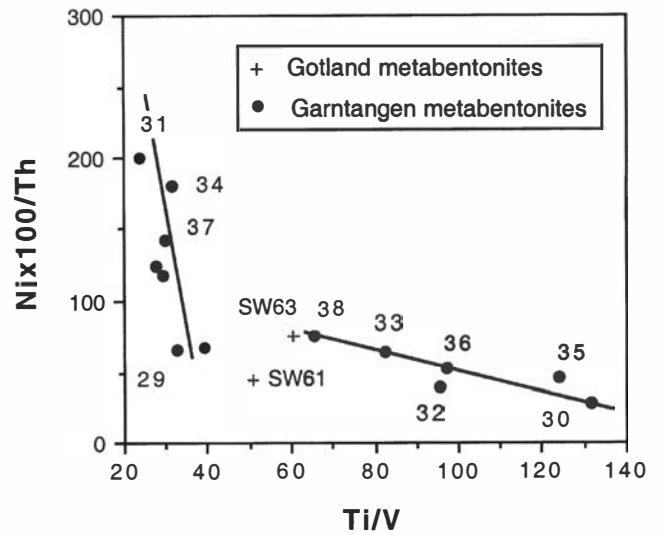


Fig. 3. Ni × 100/Th vs. Ti/V showing the association of the Gotland samples (SW61, 63) with the ‘evolved’ and ‘primitive’ Garntangen metabentonites. Data from Batchelor et al. (1995) and Batchelor & Jéppsson (1994).

between the *Pentamerus* and *Pentameroides* Biozones, which have been equated with the *M. crispus* graptolite Biozone (Worsley 1989). The extrapolated correlations of the fauna into the graptolite horizons suggest that the Norwegian Garntangen sequence is older than the Swedish, Lower Visby Formation. However, geochemical comparison of the two sequences casts doubt on the extrapolation into graptolite zones. The stratigraphical distribution of metabentonites at both localities is shown schematically in Fig. 2.

Geochemical signatures of the apatite crystals

Previous work on the geochemistry of Norwegian metabentonites from Garntangen showed the existence of two contemporaneous volcanic sources, each generating its

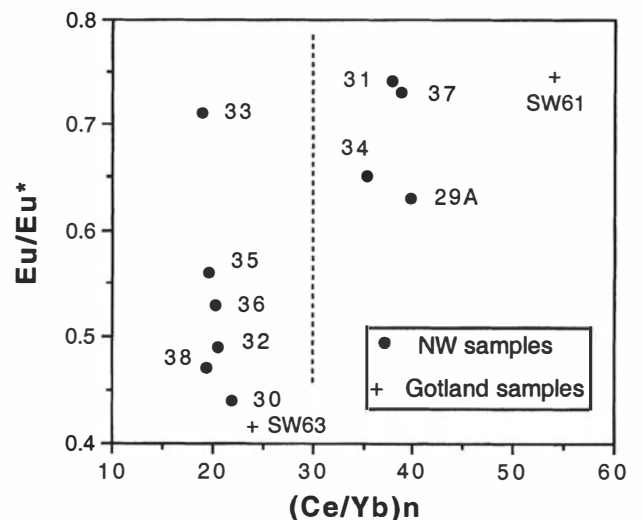


Fig. 4. (Ce/Yb)<sub>n</sub> vs. Eu/Eu\* for apatite. Data from Batchelor et al. (1995).

own distinctive magma (Batchelor et al. 1995). An evolved, mildly alkaline silica-saturated melt produced ash-containing phenocrysts of zircon, apatite and biotite, with high levels of crustal elements Zr, Nb and Th. The REE patterns of the apatite show mild LREE enrichment and strong negative europium anomalies. This group is represented by samples NW30, 32, 33, 35, 36 and 38. Sample NW33 is slightly unusual in having a weak Eu anomaly. In contrast, a more alkaline magma produced what is referred to as the 'primitive' group, which has lower concentrations of crustal elements and higher levels of Ni, Ti and V (Fig. 3). Apatite REE patterns for this group (samples NW29A, 31, 34 and 37) show stronger LREE enrichment and a generally weak Eu anomaly (Fig. 4).

Apatites from 10 metabentonites from the southern Norway Garntangen Member are compared with those of the two metabentonites from the Lower Visby Formation in Gotland, Sweden. The aim is to use Sr isotope composition as another means of comparison against which the suggested geochemical subdivisions and implied stratigraphic correlation can be assessed.

### Sr isotopes and metabentonites

The use of Sr isotope ratios to characterize apatite is a relatively new development, and, as apatite contains relatively high levels of Sr ( $10^2$ – $10^3$  ppm), it is a suitable candidate for isotopic analysis. Apatite formation in carbonatite rocks was studied by Landa et al. (1982), who used Sr isotope ratios in apatite to determine the relative contributions of crust and mantle to the genesis of mineralization, while Creaser & Gray (1992) demonstrated the stability of the Sr isotope ratios in apatite from altered Proterozoic rocks. Samson et al. (1995) were the first to apply Sr isotope analysis to Ordovician K-bentonites from the Appalachians. They showed that the Sr isotope composition was consistent within samples and was relatively immune to later alteration (which, if present, could be abraded away). They also found that there was sufficient variation in apatite Sr isotope composition to make it useful for correlative purposes.

### Analytical methods

A portion of metabentonite (ca. 100 mL) was disaggregated and washed to remove the clay component. The dry clay-free fraction was separated into light and heavy fractions using tetrabromoethane (S.G. 2.9). About 100 grains of clear, euhedral crystals of apatite, 50–200 m long, were hand-picked and submitted for Sr isotope analysis.

The apatite crystals were dissolved in 6 M HCl in 3 mL Savillex bombs overnight. The dissolved sample was dried and taken up in 2.5 M HCl. The strontium was separated using standard Dowex column separation. The Sr was run on a Finnigan 262 mass spectrometer using TaF solution

on a Re single filament to enhance emission (adapted from Birck 1986). The mass spectrometer gave an  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.710198 \pm 0.000020$  (2 S.D.) for reference sample NBS 987 (accepted value: 0.710235) during the period of analysis. All analyses achieved a precision of 0.000018 (2 S.D.).

### Sr isotope composition and magmatic affinities

Before trying to correlate different samples, it is necessary to decide at what level of error two apatite populations are the same or different. The reproducibility of the standard solution on the mass spectrometer gives a best value of  $\pm 0.002\%$  ( $2\sigma$ ). However, it is unreasonable to expect a mineral population to have such good reproducibility, since some heterogeneity might be expected in the Sr isotope composition of a population of apatites. Samson et al. (1995) analysed several apatite fractions, including single crystals, and obtained reproducibility values between 0.002% and 0.008% ( $2\sigma$ ). This is the only estimate currently available, and therefore the value 0.008% is adopted in this paper to distinguish among apatite populations. It is assumed that an age correction does not have to be made because of the low Rb/Sr ratio of apatite ( $<0.01$ ) (Samson et al. 1995).

Figure 5 displays the  $^{87}\text{Sr}/^{86}\text{Sr}$  values for apatite analyses in this study against  $1000/\text{Sr}$ . The salient points of these data are:

1. Four of the apatite samples have Sr isotope compositions between 0.7041 and 0.7045 defining the least radiogenic group, which relates to the geochemical 'primitive' group. Within this group, two pairs of samples have values that overlap within error: NW29A–SW61 and NW31–NW34.

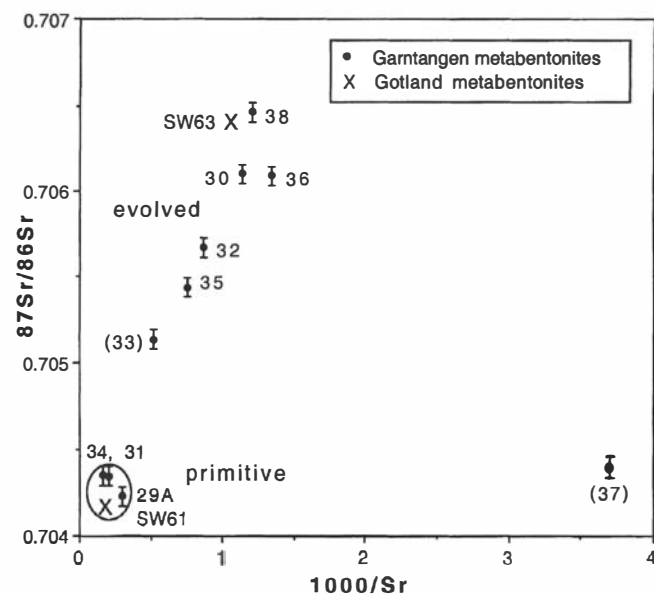


Fig. 5.  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1000/\text{Sr}$  for apatite, showing  $\pm 0.008\%$  error bars (y-axis).

Table 1. Data for  $^{87}\text{Sr}/^{86}\text{Sr}$  in apatite from Scandinavian Telychian metabentonites.

Sample	No. of grains	Measured ratio	Error (2 S.D.)
Garntangen, Oslo, Norway			
NW38	90	0.706428	$\pm 0.000006$
NW37	90	0.704739	$\pm 0.000007$
NW36	86	0.706051	$\pm 0.000007$
NW35	60	0.705400	$\pm 0.000007$
NW34	40	0.704309	$\pm 0.000006$
NW33	70	0.705091	$\pm 0.000007$
NW32	70	0.705635	$\pm 0.000005$
NW31	39	0.704312	$\pm 0.000006$
NW30	60	0.706066	$\pm 0.000009$
NW29A	39	0.704194	$\pm 0.000007$
Gotland, Sweden			
SW63	93	0.706383	$\pm 0.000007$
SW61	30	0.704130	$\pm 0.000007$
Reference sample			
NBS 987		0.710198	$\pm 0.000020$
		0.710235	(accepted value)

- Two samples, NW33 and NW37, exhibit anomalous geochemical signatures with respect to the rest of the suite. NW33 has a distinctly higher Eu/Eu\* value than the rest of the 'evolved' group (Fig. 4) and NW37 has an unusually low concentration of total Sr (Fig. 5). The Sr isotope ratio for NW33 is lower than in the rest of its geochemical group members (Table 1; Fig. 5).
- Six samples (NW30, NW32, NW35, NW36, NW38 and SW63) form the more radiogenic group, which relates to the geochemically 'evolved' group. Within error, two pairs of samples share the same Sr isotope composition: NW30–NW36 (0.7061) and NW38–SW63 (0.7064).

The range in Sr isotope composition seen in the suite of apatite from the 'evolved' group is most readily explained by differing levels of crust incorporation during formation of the parent magma from which the metabentonites were derived. Comparison with rock suites from volcanic arcs worldwide (Fig. 6) suggests similarities with the magmatism of Java and Stromboli, both of which represent active continental margins. In contrast, the 'primitive' group allies with the Philippines' and Marianas' back-arc systems (Wilson 1989).

An alternative cause of Sr isotope variation is the mixing of two apatite populations through incorporation of crystals ripped out of the country rock during eruption. Studies of zircon from bentonites suggest that it might be possible to incorporate xenocrysts during eruption, although the evidence is limited. Bowring et al. (1998) analysed 172 zircon fractions from 10 ash beds. There was evidence of an older component in some of the fractions, and they suggested, in one case, that older grains might have been incorporated during eruption. In contrast, Tucker et al. (1990) record no evidence of inherited zircon grains.

However, random incorporation of crustal material into an eruption cloud would tend to generate random variation

in bulk chemical concentration, which is clearly not the case in this study. Distribution of trace elements in the bulk sample and of REE in apatite show co-linear relationships for the 'evolved' group of metabentonites (Figs. 3, 4). In addition, lumps of crustal rock would not break down to clay in the same way as volcanic glass does, and they would therefore remain as lithic fragments within the metabentonite. No lithic fragments >1 mm were encountered during preparation of samples in this study.

Therefore the evidence from Samson et al. (1995) of Sr isotopic homogeneity in apatite from metabentonites, and the co-linearity in geochemical data distribution for the 'evolved' group lead us to conclude that the Sr isotope compositions of apatite in this study are primary and reflect the composition of the magma in which the apatite crystals grew. The data thus provide evidence that Sr isotope composition can be used in conjunction with geochemical data to help discriminate among magmatic provinces, as represented by metabentonites. In addition, the Sr isotopic ratio ranges of these apatites differ significantly from the Sr isotopic value of early Silurian sea water, which is estimated at 0.7080 (Denison et al. 1998) and therefore cannot have equilibrated with the apatite phenocrysts after deposition of the ash.

The sedimentary sequence at Garntangen in Norway thus suggests that two contemporaneous volcanic provinces were active during Telychian times, erupting almost alternately and depositing ash over this part of Baltica. However, the composition of metabentonites is not only of interest in helping to discriminate among magmatic provinces. Their use as unique time planes means

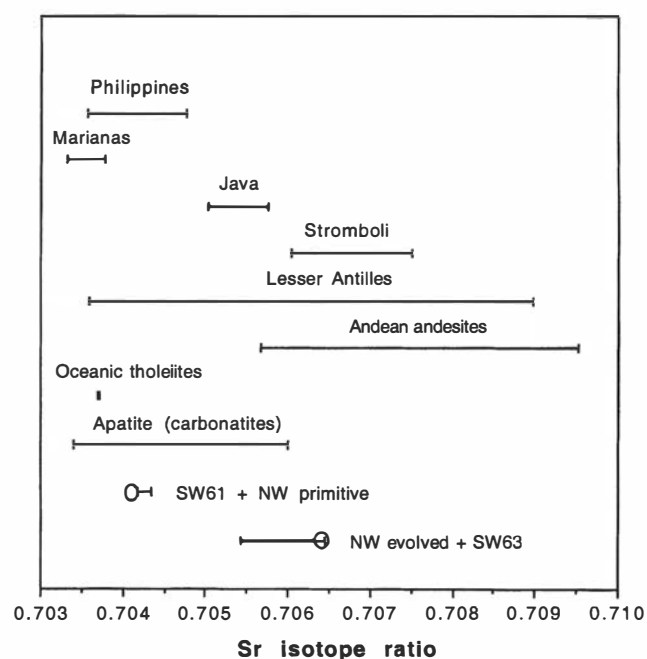


Fig. 6. Sr isotope ranges for apatite in Garntangen and Gotland samples. Data for volcanic rocks from different tectonic settings are superimposed (Landa et al. 1982; Rollinson 1993).

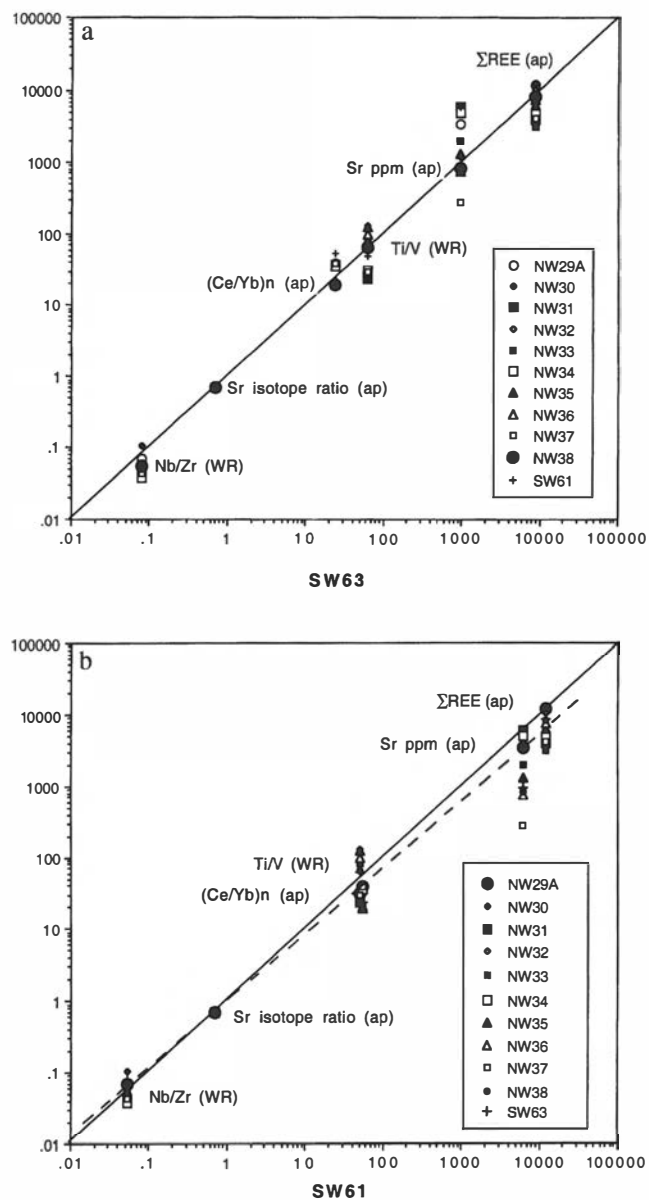


Fig. 7. (a) Correlation of the Ireviken (SW63) and Garntangen metabentonites. (b) Correlation of the Lusklint (SW61) and Garntangen metabentonites.

metabentonites are invaluable for lateral correlation of sedimentary sequences, which often have different faunal assemblages or sometimes none at all.

## Correlation

Work published on the NW and SW samples based on REE and trace elements in apatite and bulk rock (Batchelor et al. 1995) showed that the two Gotland samples (SW63 – named locally the Ireviken metabentonite, and SW61 – the Lusklint metabentonite) shared chemical characteristics with two samples from the Garntangen suite in Norway. The pairs concerned were SW63–NW38 and SW61–NW29A. Both pairs occur in the same relative stratigraphical position (Fig. 2). The Gotland pair occurs in the Lower Visby Formation, attributed to the *M. spiralis*

graptolite Biozone and *P. amorphognathoides* conodont zone (Aldridge et al. 1993), whereas the Garntangen Member metabentonites have been assigned to the *M. crispus* Biozone (Worsley 1989). The type locality for the Garntangen Member at Ringerike, where the metabentonites occur, has been correlated with the *M. greistoniensis* Biozone in Britain, but this horizon lacks conodonts. However, evidence from adjacent beds indicates a correlation with the lower part of the *P. amorphognathoides* zone (Nakrem 1986). Such discrepancies are not uncommon when attempting to cross-correlate using different faunas.

The Sr isotope data from this study provide supporting evidence for the metabentonite correlations suggested by geochemistry. The Ireviken sample from Gotland (SW63) and the Garntangen sample from Norway (NW38) have the same apatite isotope composition to the fourth decimal place, 0.70638 and 0.70642, respectively. The other pair of metabentonites, SW61 from Gotland and NW29A from Norway, correlated on the basis of geochemical composition, gives very similar isotopic values of 0.70413 and 0.70419, respectively. They are the two metabentonites with the least radiogenic apatite signatures in this study. To substantiate these comparisons, the two Gotland samples are compared to all the NW samples for a selection of trace elements in the bulk rock and apatite (Fig. 7a, b). If two or more samples share the same absolute concentrations of elements or ratios of elements, then a bivariate plot will generate a perfect correlation with a slope of 45°. The disposition of points for SW63 and NW38 defines a virtually perfect 1:1 correlation (Fig. 7a). Samples SW61 and NW29A also define a straight-line correlation, but in this case the slope is slightly less than 1 (Fig. 7b).

On the basis of this evidence, it is proposed that the Ireviken metabentonite (SW63) from Gotland correlates with the 20 mm-thick metabentonite (NW38), which occurs near the top of the Garntangen Member as exposed at Garntangen, Vik, near Oslo. Furthermore, it is suggested that the Lusklint metabentonite (SW61) from Gotland might correlate with the 100 mm-thick metabentonite (NW29) near the base of the Garntangen exposure. Since no trends of chemical evolution have been established, the evidence of temporal equivalence is less certain than the evidence of derivation from similar magmas. It is, however, proposed that the two sequences can be correlated and, as the biostratigraphical control of the Swedish section is more robust, the Garntangen section is assigned to the younger *M. spiralis* Biozone. In addition, this study has shown that the Sr isotope ratio in apatite can be of assistance in correlating altered volcanic ash horizons.

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## References

- Aldridge, R. J., Jeppsson, L. & Dorning, K. J. 1993: Early Silurian oceanic episodes and events. *Journal of the Geological Society, London* 150, 501–513.
- Batchelor, R. A. 1995: Metabentonite and tuff occurrence in Silurian greywackes at Grieston Quarry, Innerleithen, Southern Uplands. *Scottish Journal of Geology* 31, 183–185.
- Batchelor, R. A. & Clarkson, E. N. K. 1993: Geochemistry of a Silurian metabentonite and associated apatite from the North Esk Inlier, Pentland Hills. *Scottish Journal of Geology* 29, 123–130.
- Batchelor, R. A. & Jeppsson, L. 1994: Late Llandovery bentonites from Gotland, Sweden, as chemostratigraphic markers. *Journal of the Geological Society, London* 151, 741–746.
- Batchelor, R. A., Weir, J. A. & Spjeldnaes, N. 1995: Geochemistry of Telychian metabentonites from Vik, Ringerike District, Oslo Region. *Norsk Geologisk Tidsskrift* 75, 219–228.
- Birck, J. L. 1986: Precision K-Rb-Sr isotope analysis: application to Rb-Sr chronology. *Chemical Geology* 56, 73–83.
- Bowring, S. A., Erwin, D. H., Jin, Y. G., Martin, M. W., Davidek, K. & Wang, W. 1998: U/Pb zircon geochronology and tempo of the end-Permian mass extinction. *Science* 280, 1039–1045.
- Creaser, R. A. & Gray, C. M. 1992: Preserved initial  $^{87}\text{Sr}/^{86}\text{Sr}$  in apatite from altered felsic igneous rocks: a case study from the Middle Proterozoic of South Australia. *Geochimica et Cosmochimica Acta* 56, 2780–2795.
- Cope, J. C. W. 1993: High resolution stratigraphy. In Hailwood, E. A. & Kidd, R. B. (eds.): *High Resolution Stratigraphy. Geological Society of London Special Publication* 70, 257–265.
- Denison, R. E., Koepnik, R. B., Burke, W. H. & Hetherington, E. A. 1998: Construction of the Cambrian and Ordovician seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  curve. *Chemical Geology* 152, 325–340.
- Fortey, N. J., Merriman, R. J. & Huff, W. D. 1996: Silurian and late-Ordovician K-bentonites as a record of late Caledonian volcanism in the British Isles. *Transactions of the Royal Society of Edinburgh, Earth Sciences* 86, 167–180.
- Grey, J., Laufeld, S. & Boucot, A. J. 1974: Silurian trilete spores and spore tetrads from Gotland: their implications for land plant evolution. *Science* 185, 260–263.
- Kolata, D. R., Frost, J. K. & Huff, W. D. 1987: Chemical correlation of K-bentonite beds in the Middle Ordovician Decorah Subgroup, upper Mississippi valley. *Geology* 15, 208–211.
- Landa, E. A., Murina, G. A., Sheragina, Yu. P. & Krasnova, N. I. 1982: Isotopic compositions of strontium in apatite and apatite-bearing rocks of carbonate complexes. *Doklady Academy of Sciences USSR, Earth Science Section* 264, 214–216.
- Loydell, D. K. 1993: Worldwide correlation of Telychian (Upper Llandovery) strata using graptolites. In Hailwood, E. A. & Kidd, R. B. (eds.): *High Resolution Stratigraphy. Geological Society of London Special Publication* 70, 323–340.
- Nakrem, H. A. 1986: Llandovery conodonts from the Oslo region, Norway. *Norsk Geologisk Tidsskrift* 66, 121–133.
- Rollinson, H. R. 1993 *Using Geochemical Data*. Longman, London.
- Samson, S. D., Matthews, S., Mitchell, C. E. & Goldman, D. 1995: Tephrochronology of highly altered ash beds: the use of trace elements and strontium isotope geochemistry of apatite phenocrysts to correlate K-bentonites. *Geochimica et Cosmochimica Acta* 59, 2527–2536.
- Tucker, R. D., Krogh, T. E., Ross Jr, R. J. & Williams, S. H. 1990: Time-scale calibration by high precision U-Pb zircon dating of interstratified volcanic ashes in the Ordovician and Lower Silurian stratotypes of Britain. *Earth and Planetary Science Letters* 100, 51–58.
- Wilson, M. 1989 *Igneous Petrogenesis*. Chapman & Hall, London.
- Worsley, D. 1989: The Llandovery Series in the Oslo Region. In Holland, C. H. & Bassett, M. G. (eds.): *A Global Standard for the Silurian System*, 108–115. National Museum of Wales, Geological Series No. 9, Cardiff.