

SPECIAL

Syntectonic monazite in low-grade mudrocks: a potential geochronometer for cleavage formation?

P. R. WILBY¹, A. A. PAGE², J. A. ZALASIEWICZ², A. E. MILODOWSKI¹, M. WILLIAMS^{2,3} & J. A. EVANS⁴

¹British Geological Survey, Keyworth, Nottingham NG12 5GG, UK (e-mail: prwi@bgs.ac.uk)

²Department of Geology, University of Leicester, University Road, Leicester LE1 7RH, UK

³School of Earth and Environmental Sciences, University of Portsmouth, Burnaby Road, Portsmouth PO1 3QL, UK

⁴NERC Isotope Geosciences Laboratory, BGS, Keyworth, Nottingham NG12 5GG, UK

Monazite paragenesis during low-grade metamorphism is poorly understood. The first unequivocal instance of the mineral having crystallized synchronously with compressional cleavage formation is reported. Compositionally, these monazites resemble diagenetic forms but differ texturally by displaying syntectonic microfabrics. Their predominant association with organic-walled fossils implies that organic material may play an important role in controlling the behaviour of light rare earth elements (LREE) during low-grade metamorphism, probably by releasing diagenetically sequestered LREE and organically bound phosphorus during thermal maturation (devolatilization), and/or by promoting a favourable environment for monazite precipitation. Potentially, such monazites could provide a powerful geochronometer for cleavage formation.

Monazite, a light rare earth element (LREE) phosphate, crystallizes in a wide range of environments (Overstreet 1967) and is used to radiometrically date a variety of geological processes (see Parrish 1990; Scherrer *et al.* 2000, and references therein). Increasingly, it is also seen as an important tracer of REE fractionation in the rock cycle (Poitrasson *et al.* 2002). However, its contribution to the understanding of sub-amphibolite-facies metamorphism has been limited because its stability at these grades has been disputed (Overstreet 1967; Akers *et al.* 1993; Kingsbury *et al.* 1993; Ohr *et al.* 1994; Schaltegger *et al.* 1994) and such grains as are present in these rocks are often assumed to be detrital.

Recent reports of neoformed, sub-amphibolite-facies monazites (e.g. Franz *et al.* 1996; Heinrich *et al.* 1997; Cabella *et al.* 2001; Rasmussen *et al.* 2001; Wing *et al.* 2003) conflict with this notion. Typically, they consist of irregular, inclusion-rich, low-Th and low-U forms that are not readily distinguishable from diagenetic monazites (e.g. see Milodowski & Zalasiewicz 1991;

Evans & Zalasiewicz 1996). Exceptionally, they occur as minute (5–20 µm), irregular crystals, some of which are oriented parallel to the cleavage of the host rock (Kryza *et al.* 2004), or they form overgrowths whose crystal faces are aligned parallel to cleavage (Rasmussen *et al.* 2002). In no case, however, has it been possible to categorically demonstrate their growth as having been coeval with tectonism.

We report the first unequivocal evidence for monazite growth synchronous with low-temperature, compressional slaty cleavage formation.

Geological setting. The syncleavage monazites are from a quarry [SN 0024 4025] on Dinas Island, SW Wales, UK (Fig. 1). This locality exposes the late Ordovician Cwm-yr-Eglwys Mudstone Formation, which consists of organic-rich, pyritic, thinly interbedded hemipelagic and turbiditic mudstone (Davies *et al.* 2003). The unit was deposited under anoxic bottom-water conditions and contains a diverse graptolite fauna (Williams *et al.* 2003), as well as rare, organic-walled, bivalved arthropods. It forms part of the thick sedimentary fill of the Early Palaeozoic Welsh Basin.

The regional structure and metamorphic grade of the basin are well characterized (Fettes *et al.* 1985; Robinson & Bevins 1986) and the petrology and geochemistry of its mudrock-dominated fill have been examined in some detail (e.g. Dimberline 1986; Li *et al.* 1994; Ohr *et al.* 1994), particularly as regards the widespread distribution of authigenic monazites (Milodowski & Zalasiewicz 1991). The study area underwent low-grade regional metamorphism and the development of an axial-planar penetrative cleavage during the Early to Middle Devonian Acadian Orogeny (Woodcock *et al.* 1988). On a regional scale it forms part of a zone of lowermost greenschist-facies metamorphism (see Fettes *et al.* 1985; Robinson & Bevins 1986), but in detail it exhibits a complex pattern of metamorphic grades (see inset map, British Geological Survey 2003) controlled generally by lithological variations and by the positions of major faults. North of the Newport Sands Fault (see Fig. 1) the rocks are of low- to high-anchizone grade, whereas to the south they are predominantly of high-anchizone to epizone grade.

Methods. Rock slabs (BGS MWL5229 and MWL5230) and polished thin sections (BGS E74526a–d) were examined by SEM at the BGS, Keyworth (LEO 435VP) and the Department of Geology, University of Leicester (Hitachi S-3600N). The samples were imaged in backscatter mode at an accelerating voltage of 15 kV, and phases were identified by energy-dispersive X-ray microanalysis (EDXA) using Oxford ISIS X-ray and Oxford INCA X-ray analysers, respectively. Instrument detection limits for Th and U are *c.* 0.5 wt%. The slabs were examined uncoated under low-vacuum conditions; the thin sections were carbon-coated and examined under high-vacuum conditions. All material is accessioned in the BGS Collections, Keyworth, UK.

Diagenetic and detrital monazite. Diagenetic monazites are scarce and relatively small (*c.* 15 µm) in the Cwm-yr-Eglwys Mudstone Formation, but they otherwise resemble those from elsewhere in the Welsh Basin (generally <0.5–2 mm; see Milodowski & Zalasiewicz 1991) in being irregular, inclusion-rich (Fig. 2a) and low in Th and U (<0.5 wt%). Small (up to 5 µm), euhedral to subhedral, detrital monazites (Fig. 2b and h) also occur and are characterized by elevated Th and U levels (Table 1). Deflection of the cleavage fabric around both of these forms of monazite indicates that they predate Acadian metamorphism.

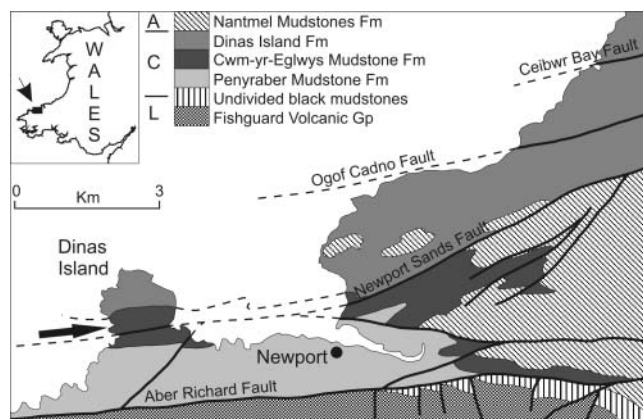


Fig. 1. Simplified geological map of the study area showing the collection site (arrowed). A, Ashgill; C, Caradoc; L, Llanvirn.

Synclavage monazite. Unzoned, low-Th and low-U (<0.5 wt%; Table 1), neoformed monazite occurs predominantly in association with organic-walled fossils (graptolites and bivalved arthropods) and less commonly as smaller crystals in association with pre-existing monazite grains. None has been observed in association with other detrital or diagenetic phases or their strain-fringes. These monazites display five distinctive microtextures that unequivocally link them to cleavage formation, as follows.

Replacement (Fig. 2c). Monazites, ranging from small, dispersed crystals (<1 μm diameter) to larger composite masses (≤ 60 μm diameter), replace tectonically fragmented particles of fossil cuticle. Although the fragments themselves exhibit little evidence of internal strain, the neoblasts are oriented parallel to the direction of principal stress.

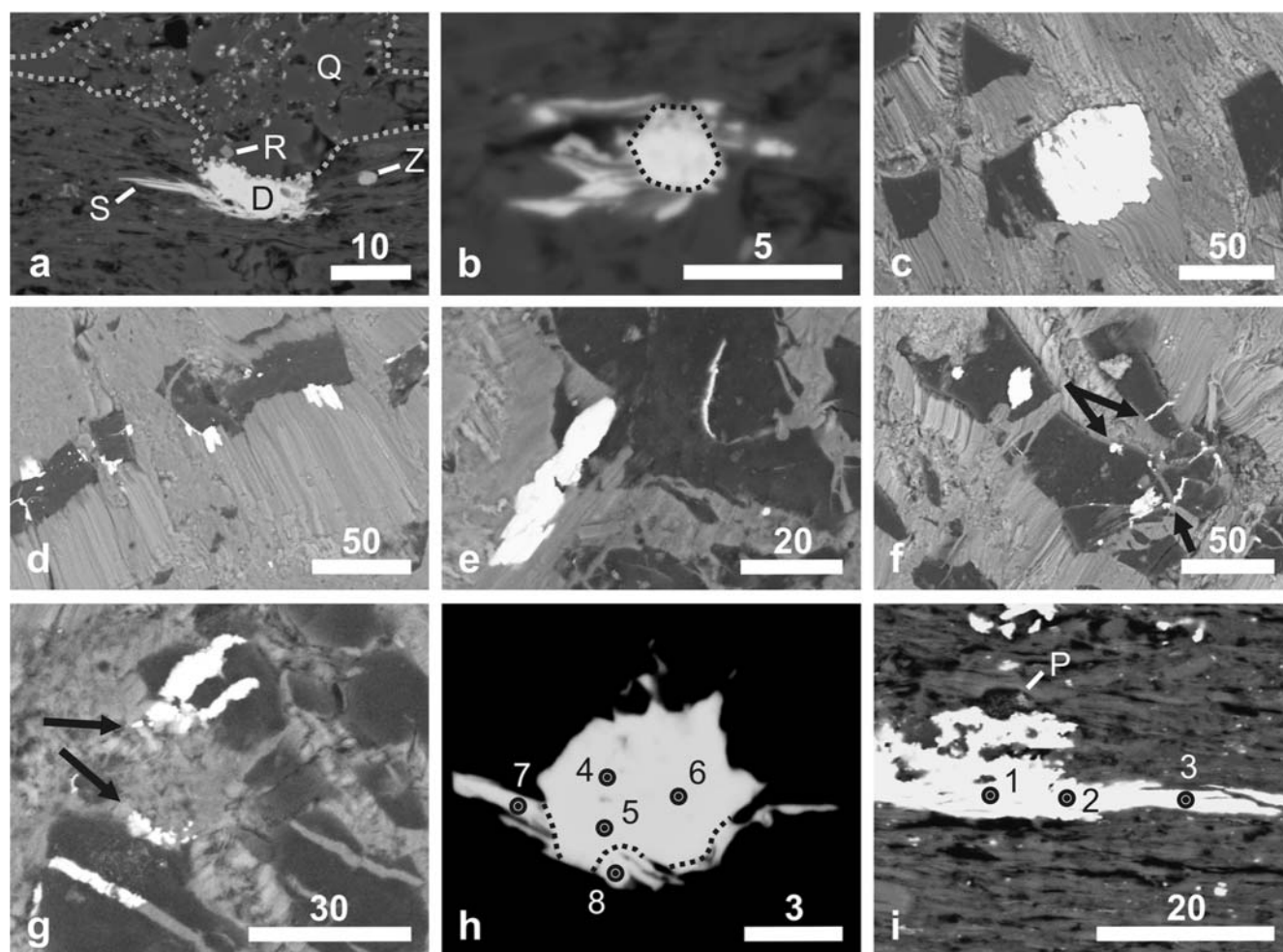


Fig. 2. (a–i) High-contrast, backscattered SEM images of synclavage monazites (white); scale bars in microns. (a) Elongate outgrowths (S) into the cleavage from an irregular, inclusion-rich diagenetic monazite (D). (Note rutile (R) and zircon (Z) are unaffected.) Minute monazites define the boundaries of crystals in an associated quartz strain-fringe (Q, outlined). (b) Outgrowths into the cleavage from a euhedral detrital monazite (outlined). (c–g) Monazites associated with tectonically fragmented cuticle (black) and accompanying chlorite–white mica strain-fringes (pale grey). (c) Cuticle fragment replaced by a composite monazite; individual crystals are structurally aligned. (d, e) Monazites intergrown with strain-fringe micas. (f, g) Monazites filling incipient cracks that have been bisected (arrowed) by subsequent strain. (h, i) Monazites analysed by EDXA (see Table 1). (h) Detrital monazite (outlined) with synclavage outgrowths. (i) Synclavage monazite in rock matrix. P, pyrite.

Table 1. Representative syncleavage and detrital monazite compositions (wt%) by EDXA

Analysis	1	2	3	4*	5*	6*	7	8
P ₂ O ₅	33.62	32.08	35.35	34.57	34.45	32.28	34.52	32.96
CaO	1.06	1.51	1.31	2.16	1.87	2.61	1.63	1.3
La ₂ O ₃	17.32	19.6	15.56	13.21	13.63	16.74	18.91	19.56
Ce ₂ O ₃	32.99	32.44	35.1	35.8	33.66	32.47	33.04	34.55
Nd ₂ O ₃	12.97	12.17	13.82	11.96	13.21	13.38	12.96	10.39
Sm ₂ O ₃	0.4	1.33	0.83	bd	1.11	bd	bd	0.52
ThO ₂	bd	bd	bd	1.59	1.33	3.31	bd	bd
UO ₂	bd	bd	bd	0.68	0.7	bd	bd	bd
Total	98.36	99.13	101.97	99.97	99.96	100.79	101.06	99.28

bd, below detection limit.

*Detrital monazite compositions.

Strain-fringe intergrowth (Fig. 2d and e). Idioblasts of monazite ($\leq 50 \mu\text{m}$ long) extend from the edges of cuticle fragments into their associated strain-fringes, where they are interleaved with chlorite–white mica stacks.

Fracture-filling (Fig. 2f and g). Incipient tectonic fractures within the fossils are filled with monazites. Locally, these have been bisected by continued dilation.

Outgrowth (Fig. 2a–b and h). Elongate monazites ($\leq 15 \mu\text{m}$ long) project from the surfaces of pre-existing monazites into the surrounding matrix, parallel to the cleavage fabric.

Crystal boundary (Fig. 2a). Minute monazite inclusions occur in quartz strain-fringes associated with pre-existing monazites. Many of the inclusions are clustered into short, discrete arrays that define the boundaries of adjacent quartz crystals, or occur near the edge of the strain-fringe.

Behaviour of LREE. The behaviour of LREE and the reactions responsible for monazite growth during metamorphism are poorly understood. Detrital and/or diagenetic monazites are considered the dominant reservoir(s) of LREE in sub-amphibolite-facies mudrocks (Burnotte *et al.* 1989; Milodowski & Zalasiewicz 1991); other significant reservoirs include apatite, clay minerals, iron and manganese oxides, hydrous LREE phosphates, xenotime and other detrital heavy minerals (see Ohr *et al.* 1994; Schaltegger *et al.* 1994; Rasmussen 1996, and references therein). These phases are widely believed to constitute the direct or indirect precursors to metamorphic monazites (see Smith & Barreiro 1990; Akers *et al.* 1993; Kingsbury *et al.* 1993). None, however, adequately accounts for the spatial distribution and composition of the syncleavage monazites. All are neoblastic and show no evidence of being pseudomorphs after a precursor phase. Compositional differences (particularly Th and U, Table 1) between syncleavage outgrowths and their associated detrital monazites indicate that the neoblasts are not products of local strain-induced dissolution and reprecipitation. Further, there is no indication that the neoblasts' constituents were derived from the rock matrix: the monazites are notably absent from the majority of strain-fringes despite the fact that these areas represented regions of enhanced recrystallization and high fluid flux where LREE and/or P could potentially have been exsolved or concentrated during metamorphism (see Franz *et al.* 1996; Cabella *et al.* 2001).

Instead, petrographic evidence indicates a close spatial correlation between monazite crystallization and organic material. Although syncleavage monazites are present within the rock matrix (Fig. 2i), they are sparse and typically very small (usually

$< 10 \mu\text{m}$ long); the vast majority and the largest monazites are closely associated with organic-walled fossils. The potential role of organic material in moderating the behaviour of LREE during low-grade metamorphism has previously been overlooked, although it is known to be important in the sedimentary and diagenetic realms (e.g. see Ohr *et al.* 1994; Seredin 1996). Milodowski & Zalasiewicz (1991) assigned the widespread formation of diagenetic monazites in the Welsh Basin to the wholesale migration of REE out of turbidite muds into adjacent hemipelagic horizons, where they were concentrated by organic complexation. Diagenetic monazites are sparse in the Cwm-yr-Eglwys Mudstone Formation and much of the sediment's LREE budget could conceivably have been retained by organic material into the metamorphic realm. It is postulated that under such conditions monazite crystallization was initiated by the coeval liberation of LREE and organically bound P from the fossils in response to syncleavage graphitization, perhaps catalysed by the expulsion of volatiles.

Preferential development of monazites in association with discrete organic particles (fossils) over dispersed organic detritus is probably a function of LREE mobility. These elements are fairly immobile during metamorphism, perhaps migrating only over distances of several hundred micrometres to tens of millimetres (Kingsbury *et al.* 1993; Franz *et al.* 1996; Heinrich *et al.* 1997). They are, therefore, unlikely to have been able to reach sufficient concentrations at any one point from dispersed sources to prompt widespread monazite crystallization in the background sediment.

Discussion. Low-grade metamorphic events have proved difficult to date, principally because of the paucity of suitable neoformed radiogenic minerals. Currently available techniques, based on K–Ar, Rb–Sr and ^{40}Ar – ^{39}Ar analyses of clays (e.g. Merriman *et al.* 1995; Evans 1996; Sherlock *et al.* 2003), are susceptible to: (1) thermal isotopic resetting; (2) contamination by alteration products and detrital constituents; (3) uncertainty about mineralogical relationships and initial isotopic compositions. The reliability of another technique, based on Sm–Nd analyses of paired phases, is dependent upon the two phases having crystallized closely in time and having equilibrated with the same fluid (e.g. Ohr *et al.* 1994); criteria that are not always met (Evans & Zalasiewicz 1996).

Monazite represents a potentially important alternative geochronometer. It has a high closure temperature for the U–Pb, Th–Pb and Pb–Pb decay systems (Cherniak *et al.* 2004), is easily distinguished from detrital constituents, and is resistant to alteration. Recognition of pure syncleavage monazite opens the possibility of radiometrically constraining low-grade cleavage

formation events and, in combination with co-occurring diagenetic monazites, of using a single mineral to track the diagenetic–metamorphic transition in mudrocks. Although typically small and low in Th and U, these monazites are of comparable size and composition with other low-temperature forms from which high-precision dates have been obtained (e.g. Evans *et al.* 2002; Rasmussen *et al.* 2002).

Conclusions. Accurate determinations of monazite paragenesis rely on understanding textural relationships. Those described here unequivocally link crystallization to (Acadian) cleavage formation under sub-amphibolite-facies conditions. This extends the range of environments in which monazite is known to form and suggests that the mineral could find widespread application as a geochronometer for low-temperature deformation events. Recognition of syncleavage monazite emphasizes the dangers of uncritically assigning a detrital origin to relict crystals (domains) in polyphase grains from high-grade metapelites.

The localized development of the monazites indicates that organic material may be more important in controlling the distribution and behaviour of LREE in mudrocks during sub-amphibolite-facies metamorphism than hitherto suspected. In contrast, detrital and diagenetic monazites remain relatively stable under such conditions.

We thank R. Wilson for assisting with SEM analyses, and R. J. Merriman and S. R. Noble for constructive comments.

References

- AKERS, W.T., GROVE, M., HARRISON, T.M. & RYERSON, F.J. 1993. The instability of rhabdophane and its unimportance in monazite paragenesis. *Chemical Geology*, **110**, 169–176.
- BRITISH GEOLOGICAL SURVEY 2003. *Cardigan and Dinas Island, Solid and Drift Geology. Sheet 193, England and Wales 1:50 000 scale map series*. British Geological Survey, Nottingham.
- BURNOTTE, E., PIRARD, E. & MICHEL, G. 1989. Genesis of grey monazite: evidence from the Palaeozoic of Belgium. *Economic Geology*, **84**, 1417–1429.
- CABELLA, R., LUCCHETTI, G. & MARESCOTTI, P. 2001. Authigenic monazite and xenotime from pelitic metacherts in pumpellyite–actinolite-facies conditions, Sestri–Votaggio Zone, central Liguria, Italy. *Canadian Mineralogist*, **39**, 717–727.
- CHERNIAK, D.J., WATSON, E.B., GROVE, M. & HARRISON, T.M. 2004. Pb diffusion in monazite: a combined RBS/SIMS study. *Geochimica et Cosmochimica Acta*, **68**, 829–840.
- DAVIES, J.R., WATERS, R.A., WILBY, P.R., WILLIAMS, M. & WILSON, D. 2003. *The Cardigan and Dinas Island district—a brief explanation of the geology, 1:50 000 Series England and Wales Sheet 193 (including part of Sheet 210)*. British Geological Survey, Keyworth.
- DIMBERLINE, A.J. 1986. Electron microscope and microprobe analysis of chlorite–mica stacks in the Wenlock turbidites, mid Wales, U.K. *Geological Magazine*, **123**, 299–306.
- EVANS, J.A. 1996. Dating the transition of smectite to illite in Palaeozoic mudrocks using the Rb–Sr whole-rock technique. *Journal of the Geological Society, London*, **153**, 101–108.
- EVANS, J.A. & ZALASIEWICZ, J.A. 1996. U–Pb, Pb–Pb and Sm–Nd dating of authigenic monazite: implications for the diagenetic evolution of the Welsh Basin. *Earth and Planetary Science Letters*, **144**, 421–433.
- EVANS, J.A., ZALASIEWICZ, J.A., FLETCHER, I., RASMUSSEN, B. & PEARCE, N.G. 2002. Dating diagenetic monazite in mudrocks: constraining the oil window? *Journal of the Geological Society, London*, **159**, 619–622.
- FETTES, D.J., LONG, C.B. & BEVINS, R.E. *ET AL.* 1985. Grade and time of metamorphism in the Caledonide Orogen of Britain and Ireland. In: HARRIS, A.L. *ET AL.* (ed.) *The Nature and Timing of Orogenic Activity in the Caledonian Rocks of the British Isles*. Geological Society, London, Memoirs, **9**, 41–53.
- FRANZ, G., ANDREHS, G. & RHEDE, D. 1996. Crystal chemistry of monazite and xenotime from Saxothuringian–Moldanubian metapelites, NE Bavaria, Germany. *European Journal of Mineralogy*, **8**, 1097–1118.
- HEINRICH, W., ANDREHS, G. & FRANZ, G. 1997. Monazite–xenotime miscibility gap thermometry. I. An empirical calibration. *Journal of Metamorphic Geology*, **15**, 3–16.
- KINGSBURY, J.A., MILLER, C.F., WOODEN, J.L. & HARRISON, T.M. 1993. Monazite paragenesis and U–Pb systematics in rocks of the eastern Mojave Desert, California, U.S.A.: implications for thermochronometry. *Chemical Geology*, **110**, 147–167.
- KRYZA, R., ZALASIEWICZ, J.A., CHARNLEY, N., MIŁODOWSKI, A.E., KOSTYLEW, J. & TYSZKA, R. 2004. *In situ* growth of monazite in anchizonal to epizonal mudrocks: first record from the Variscan accretionary prism of the Kaczawa Mountains, West Sudetes, SW Poland. *Geologica Sudetica*, **36**, 39–51.
- LI, G., PEACOR, D.R., MERRIMAN, R.J., ROBERTS, B. & VAN DER PLUIM, B.A. 1994. TEM and AEM constraints on the origin and significance of chlorite–mica stacks in slates: an example from central Wales. *Journal of Structural Geology*, **16**, 1139–1157.
- MERRIMAN, R.J., REX, D.C., SOPER, N.J. & PEACOR, D.R. 1995. The age of Acadian cleavage in northern England, U.K.: K–Ar and TEM analysis of a Silurian metabentonite. *Proceedings of the Yorkshire Geological Society*, **50**, 255–265.
- MIŁODOWSKI, A.E. & ZALASIEWICZ, J.A. 1991. Redistribution of rare earth elements during diagenesis of turbidite/hemipelagite mudrock sequences of Llandovery age from central Wales. In: MORTON, A.C., TODD, S.P. & HAUGHTON, P.D.W. (eds) *Developments in Sedimentary Provenance Studies*. Geological Society, London, Special Publications, **57**, 101–124.
- OHR, M., HALLIDAY, A.N. & PEACOR, D.R. 1994. Mobility and fractionation of rare earth elements in argillaceous sediments: implications for dating diagenesis and low-grade metamorphism. *Geochimica et Cosmochimica Acta*, **58**, 289–312.
- OVERSTREET, W.C. 1967. *The Geological Occurrence of Monazite*. US Geological Survey, Professional Papers, **530**.
- PARRISH, R.R. 1990. U–Pb dating of monazite and its application to geological problems. *Canadian Journal of Earth Science*, **27**, 1431–1450.
- POITRASSEN, F., HANCHAR, J.M. & SCHALTEGGER, U. 2002. The current state and future of accessory mineral research. *Chemical Geology*, **191**, 3–24.
- RASMUSSEN, B. 1996. Early diagenetic REE-phosphate minerals (florencite, gorceixite, crandallite and xenotime). *American Journal of Science*, **296**, 601–632.
- RASMUSSEN, B., FLETCHER, I.R. & McNAUGHTON, N.J. 2001. Dating low-grade metamorphic events by SHRIMP ion analysis of monazite in shales. *Geology*, **29**, 963–966.
- RASMUSSEN, B., BENGTON, S., FLETCHER, I.R. & McNAUGHTON, N.J. 2002. Discoidal impressions and trace-like fossils more than 1200 million years old. *Science*, **296**, 1112–1115.
- ROBINSON, D. & BEVINS, R.E. 1986. Incipient metamorphism in the Lower Palaeozoic marginal basin of Wales. *Journal of Metamorphic Geology*, **4**, 101–113.
- SCHALTEGGER, U., STILLE, P., RAIS, N., PIQUÉ, A. & CLAUER, N. 1994. Neodymium and strontium isotopic dating of diagenesis and low-grade metamorphism of argillaceous sediments. *Geochimica et Cosmochimica Acta*, **58**, 1471–1481.
- SCHERRER, N.C., ENGI, M., GNOS, E., JAKOB, V. & LIECHTI, A. 2000. Monazite analysis: from sample preparation to microprobe age dating and REE quantification. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **80**, 93–105.
- SEREDIN, V.V. 1996. Rare earth element-bearing coals from the Russian Far East deposits. *International Journal of Coal Geology*, **30**, 101–129.
- SHERLOCK, S.C., KELLEY, S.P., ZALASIEWICZ, J.A., SCHOFIELD, D.I., EVANS, J.A., MERRIMAN, R.J. & KEMP, S.J. 2003. Precise dating of low-temperature deformation: strain-fringe analysis by ^{40}Ar – ^{39}Ar laser microprobe. *Geology*, **31**, 219–222.
- SMITH, H.A. & BARREIRO, B. 1990. Monazite U–Pb dating of staurolite grade metamorphism in pelitic schists. *Contributions to Mineralogy and Petrology*, **105**, 602–615.
- WILLIAMS, M., DAVIES, J.R., WATERS, R.A., RUSHTON, A.W.A. & WILBY, P.R. 2003. Stratigraphical and palaeoecological importance of Caradoc (Upper Ordovician) graptolites from the Cardigan area, southwest Wales. *Geological Magazine*, **140**, 549–571.
- WING, B.A., FERRY, J.M. & HARRISON, T.M. 2003. Prograde destruction and formation of monazite and allanite during contact and regional metamorphism of pelites: petrology and geochronology. *Contributions to Mineralogy and Petrology*, **145**, 228–250.
- WOODCOCK, N.H., AWAN, M.A., JOHNSON, T.E., MACKIE, A.H. & SMITH, R.D.A. 1988. Acadian tectonics of Wales during Avalonia/Laurentia convergence. *Tectonics*, **7**, 483–495.