Chapter 13

GEOCHEMISTRY OF HEAVY MINERALS

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ABSTRACT

This contribution provides an insight into the use of mineral chemistry in provenance research, and demonstrates how studies, by using microbeam techniques on several detrital heavy mineral species, benefit from continuing technological advances. Virtually all detrital heavy minerals can now be subjected to sophisticated geoanalytical techniques that can determine their major and trace element compositions and identify their crystal chemistry. Petrogenetic controls impart distinctive elemental signatures to mineral phases in igneous and metamorphic rocks that are preserved in mineral grains eroded from them, and can be used as a genetic tool to help decode their parageneses. Of particular interest are those heavy minerals that are widespread in sediments with compositions that are suitable for routine geochemical analysis. In this review, the geochemistry of garnet, tourmaline, chrome spinel, apatite, pyroxenes and amphiboles and its application to specific geological problems is discussed in detail; brief references are given to minerals that have not been used frequently in provenance studies. It is important to emphasise that a particular species, chosen for geochemistry, is generally associated with other minerals that are also carriers of information. Therefore, mineral chemical data need to be integrated with information from the whole assemblage to ensure that the conclusions are truly comprehensive.

Keywords: heavy mineral chemistry; single mineral (varietal) analysis; microbeam techniques; garnet; tourmaline; apatite; chrome spinel

1. INTRODUCTION

Quantifying the characteristics of a single mineral (single-mineral analysis) is now frequently applied to increase confidence in detrital mineral studies and to add detail

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unavailable from conventional heavy mineral analyses. Single-mineral (varietal) analytical methods are extremely diverse but fall into three main categories: petrographic, isotopic and geochemical.

Petrographic characteristics include parameters such as colour, shape, habit, and zoning patterns. For example, zircon morphology has long been regarded as a petrogenetic indicator (Pupin and Turco, 1981; Corfu, 2001; Corfu et al., 2003). Colour varieties of minerals such as zircon and tourmaline are known to be provenance-diagnostic (Mackie, 1923; Krynine, 1946; Mange-Rajetzky, 1995). Apatite morphology has been used to evaluate sediment transport history, for example in Devonian-Carboniferous sandstones of the Clair Field, west of Shetland (Allen and Mange-Rajetzky, 1992).

Radiogenic methods are being used with increasing frequency, including fission track dating of zircons and apatites and U-Pb dating of phases such as detrital zircon, monazite and titanite. The study of isotopic systems is beyond the scope of this chapter, however, zircon and apatite fission track analysis (ZFTA, AFTA), which has a long history of application in sedimentary basins, is outlined here by Carter (2007 – this volume). Isotopic analysis of zircon in provenance studies is reviewed by Fedo et al. (2003).

Geochemical analysis, using a variety of microbeam techniques, has been applied to a large range of detrital heavy mineral species, including garnet, chrome spinel, tourmaline, amphiboles, pyroxenes, zircon, apatite, ilmenite and rutile. The objective of this contribution is to provide an insight into the use of mineral chemistry in sedimentary research, and how this has benefited from continuing technological advances. Almost all detrital heavy minerals can now be subjected to a range of sophisticated geoanalytical techniques that can determine their major and trace element compositions and identify their crystal chemistry. Petrogenetic controls impart distinctive elemental signatures to mineral phases in igneous and metamorphic rocks. These are preserved in detrital mineral grains derived from them, and can be used as a genetic tool to help decode their paragenesis. Of particular interest are those heavy minerals that are most widespread in sediments with compositions suitable for routine geochemical analysis. In this review, garnet, tourmaline, chrome spinel, apatite, pyroxenes and amphiboles are discussed in detail, while brief references are given to minerals that have not been used frequently in provenance studies.

It is important to emphasise that heavy mineral assemblages are relatively diverse, and the particular species chosen for geochemistry is associated with other minerals that are also carriers of information. Therefore, the mineral chemical data need to be integrated with information from the whole assemblage to ensure that the conclusions are truly comprehensive.

2. HISTORICAL OVERVIEW

With the advent of increasingly sophisticated microanalytical techniques in the latter part of the last century, mineral chemical analysis has become an integral part of many heavy mineral provenance studies. The earliest mineral chemical provenance studies (e.g., Luepke, 1980) were undertaken by atomic absorption analysis.

Because this technique requires relatively large amounts of sample, analysis was conducted on bulk separates. Although such studies were pioneering in their day, the conclusions that can be drawn from them were limited, because the data represent an averaged signal from a wide variety of potential source rocks. Geochemical analysis of mineral separates, therefore, at best gives only an imprecise view of provenance, and can, at worst, be seriously misleading. This approach was rapidly superseded by single-grain microbeam methods, particularly electron microprobe analysis, which became widely available in the 1980s, spawning a series of works on the geochemistry of a variety of mineral species, such as amphibole (Mange-Rajetzky and Oberhänsli, 1982), clinopyroxene (Cawood, 1983), tourmaline (Henry and Guidotti, 1985), garnet (Morton, 1985), zircon (Owen, 1987) and chrome spinel (Press, 1986).

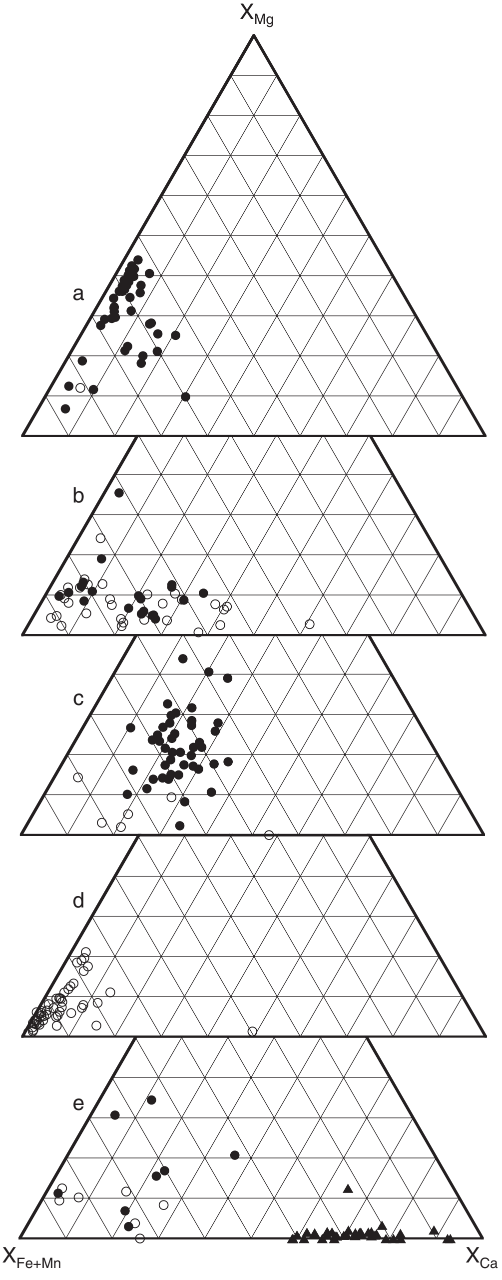
More recently, yet more sophisticated technology has been developed, such as the sensitive high-resolution ion microprobe (SHRIMP) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS), which enable high-precision determination of trace elements and isotopic compositions of single-mineral grains. Although the main application of such techniques has been in radiometric dating of detrital heavy minerals such as zircon and monazite, they have also been used for mineral-chemical studies, either to provide trace element data on minerals more commonly analysed by electron microprobe, such as garnet (Čopjaková et al., 2005), or on minerals that show little major element variation, such as zircon (Belousova et al., 2002a) and apatite (Morton and Yaxley, 2007).

3. HEAVY MINERALS USED FREQUENTLY FOR GEOCHEMICAL ANALYSIS

3.1. Garnet

Garnet geochemistry is the most widely used mineral-chemical tool for determination and discrimination of sediment provenance, for several reasons. Firstly, it is a common component of many heavy mineral assemblages. Secondly, garnet is a relatively stable mineral under both weathering and burial diagenetic conditions (Morton and Hallsworth, 1999; Morton and Hallsworth, 2007, this volume), and, most importantly, it shows a wide range in major element compositions, enabling easy acquisition of mineral-chemical data using readily available electron microprobe facilities. Garnet is especially interesting in that it varies not only by bulk composition (protolith), but also P and T of formation, in both igneous and metamorphic rocks. In the latter, it often preserves the metamorphic path, i.e., the growth during changing P-T conditions, which can be particularly diagnostic. Most naturally-occurring garnets correspond to the general formula $(Mg,Fe^{2+},Mn,Ca)_3(Al,Cr,Ti,Fe^{3+})_2Si_3O_{12}$, but there are several other possible substitutions (Deer et al., 1997). Garnets fall into two isomorphous series: pyralspite $[(Mg,Fe^{2+},Mn)_3Al_2Si_3O_{12}]$ and ugrandite $[Ca_3(Al,Cr,Ti,Fe^{3+})_2Si_3O_{12}]$. Variations within the individual series are fairly complete and continuous, but there is no evidence for continuous variation between the two series.

The first paper to show the potential of garnet geochemistry as a provenance indicator was by Morton (1985). Since then, garnet geochemical constraints on sediment provenance have been included in a large number of papers dealing with sediments from the Palaeozoic to the Holocene in sedimentary basins worldwide, among them being the Devonian of the Midland Valley of Scotland (Haughton and Farrow, 1988), the Carboniferous of the Culm Basin, Czech Republic (Hartley and Otava, 2001), Permian to Jurassic sandstones of the southern Kitakami Terrane,



Japan (Takeuchi, 1994), the Triassic of the Barents Shelf, north of Norway (Mørk, 1999), Cretaceous to Palaeocene sandstones from the Polish Western Carpathians (Oszczypko and Salata, 2005), Jurassic to Cretaceous sandstones of Papua New Guinea (Morton et al., 2000), Cretaceous sandstones of the eastern Alps (Von Eynatten and Gaupp, 1999), Eocene to Oligocene sandstones from offshore New Zealand (Smale and Morton, 1987), Pliocene sandstones from the Southern Caspian Basin, Azerbaijan (Morton et al., 2003a), Miocene to Quaternary sandstones from the Bengal Fan (Yokoyama et al., 1990) and modern river sediments in the Netherlands (Tebbens et al., 1995).

The wide variety of garnet populations found in sandstones (Fig. 1) clearly illustrates how useful garnet assemblages are for distinguishing sandstones from different sources. However, using these data to reconstruct source area lithology is more problematic, since different parageneses may contain similar garnets. For instance, Wright (1938) showed that there is strong overlap between garnets from biotite schists and amphibolites, and between amphibolites and eclogites (Fig. 2). Morton et al. (2004) suggested that this problem could be overcome by using a deterministic approach that characterises the garnet assemblages from different potential sources by analysing assemblages from modern river sediment. They used these data to tie garnet assemblages in ancient sandstones back to specific source regions. One of the main outcomes of this work was to demonstrate that amphibolite facies metasedimentary terrains supply garnet assemblages with low Mg and variable Ca, which they termed Type B (Fig. 3). By contrast, high-grade mafic and ultramafic gneisses provide detrital garnet assemblages rich in high-Mg, high-Ca garnets, termed Type C (Fig. 3). Garnets from ultramafic rocks such as pyroxenites and peridotites have higher Mg contents than those from metabasic rocks (Morton et al., 2004). In western Norway, for example, garnets in pyroxenites and peridotites have $X_{\mathrm{Mg}} > 50\%$, whereas most garnets from metabasic rocks have $X_{\mathrm{Mg}} < 40\%$ (Fig. 4). A subdivision of Type C garnets into Ci ($X_{\mathrm{Mg}} < 40\%$) and Cii ($X_{\mathrm{Mg}} > 40\%$) may therefore be useful in assessing the relative contributions from mafic and ultramafic metamorphic sources (Fig. 5).

Fig. 1. Variations in garnet compositions illustrating the value of garnet geochemical analysis as a discriminator of sandstone provenance. (a) Triassic sandstone from the Strathmore Field, west of Shetland, UK (Well 205/26a-2, 2596.5 m), dominated by high-Mg, low-Ca garnets, derived from a high-grade (granulite facies) metasedimentary or charnockitic terrain (Morton et al., 2007, this volume). (b) Palaeocene sandstone from the Gannet area, central North Sea, UK (Well 21/30-13, 2279.6 m), containing low-Mg garnets with variable Ca, derived from amphibolite facies Dalradian metasediments of Scotland (Morton et al., 2004). (c) Palaeocene sandstone from the Ormen Lange area, Møre Basin, Norway (Well 6306/10-1, 1190.7 m), derived from high-grade metabasic rocks of western Norway (Morton et al., 2004). (d) Oligocene sandstone from the Georgian Republic, Asia (CASP sample WG95/1), containing high-Mn, low-Mg and low-Ca garnets, derived from granitoids in the Dzirhuli Massif. (e) Pliocene sandstone from Babazanan, Azerbaijan, containing Fe^{3+}-Ca-rich garnets derived from very low-grade metabasic rocks in the Lesser Caucasus (Morton et al., 2003a). X_{Fe}, X_{Mg}, X_{Ca}, X_{Mn} = ionic contents of Fe, Mg, Ca and Mn respectively, calculated on the basis of 24 oxygens, and normalised to total Fe + Mg + Ca + Mn, as recommended by Droop and Harte (1995). All Fe calculated as Fe^{2+}. Filled circles, garnets with $X_{\mathrm{Mn}} < 5\%$; open circles, garnets with $X_{\mathrm{Mn}} > 5\%$; triangles, garnets with $Fe^{3+}/Al > 0.10$.

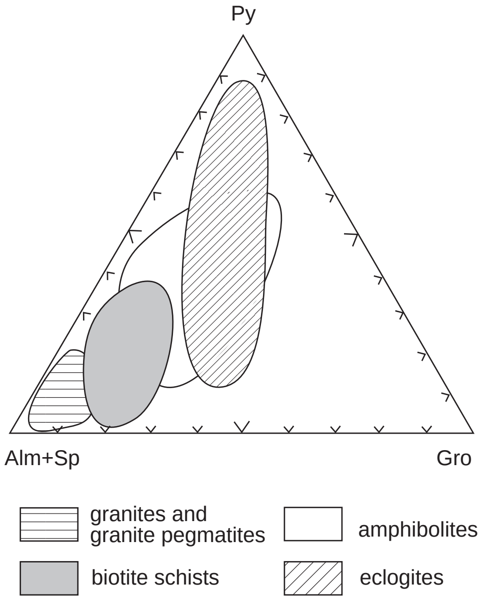


Fig. 2. Range of garnet compositions from granites and granite pegmatites, biotite schists, amphibolites and eclogites, adapted from Wright (1938) and Preston et al. (2002).

Type A garnet assemblages, which have high Mg and low Ca (Fig. 2) are generally attributed to high-grade (granulite facies) metasedimentary rocks or charnockites (Sabeen et al., 2002; Morton et al., 2004). However, Hamer and Moyes (1982) reported similar garnets from xenocrysts and in xenoliths in intermediate-acidic igneous rocks of the Antarctic Peninsula, where they represent metamorphic material incorporated into the magma at deep crustal levels. Type A garnets have also been recorded as phenocryst phases in intermediate-acidic igneous rocks (Green and Ringwood, 1968; Fitton, 1972), resulting from direct crystallisation from acid calc-alkaline magma at pressures of $0.9–1.8 \times 10^9$ Pa. Therefore, Type A garnets can be derived from intermediate-silicic igneous rocks that are the products of magmas emanating from deep crustal levels. Integrating heavy mineral data with garnet geochemical data would readily enable a distinction of the two alternative sources of Type A garnet, because assemblages derived from high-grade metasedimentary rocks or charnockites have markedly different characteristics to those derived from a predominantly igneous terrain.

Detrital garnet assemblages with low abundances of Types A, B and C have been found in a variety of circumstances, for example, in Pliocene to Holocene sediments from the South Caspian Basin, Azerbaijan (Fig. 1). Sediments transported by both the modern Kura and palaeo-Kura river systems, sourced from the Lesser Caucasus mountain range, are characterised by abundant Fe^{3+}-Ca (andradite-grossular) garnets (Fig. 1). Such garnets are here termed 'Type D'. The most typical occurrence of Type D garnets is in contact or thermally metamorphosed calcareous sediments, and especially in associated metasomatic skarns (Deer et al., 1997). However, such a provenance is unlikely in the case of the Kura and palaeo-Kura assemblages, since

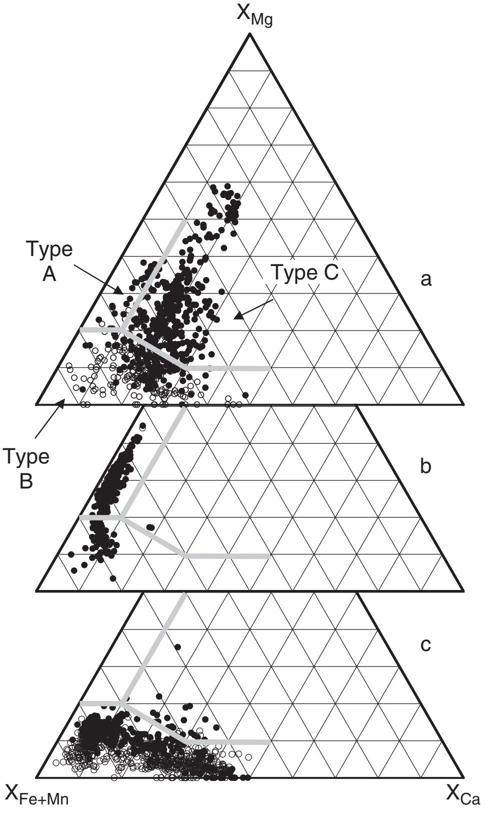


Fig. 3. Garnets in modern river and beach sediments, illustrating the close relationship between detrital garnet compositions and their source rocks. (a) Sediments from rivers draining the Western Gneiss Region of western Norway, an area with widespread high grade basic gneisses (from Morton et al., 2004). Note the abundance of garnets corresponding to Type C (high Ca, high Mg). (b) Sediments from beaches and rivers in southern India, an area comprising high grade (granulite facies) metasediments and charnockites (from Sabeen et al., 2002). Note the abundance of Type A garnet (low Ca, high Mg). (c) Sediments from rivers draining Moine metasediments of the Northern Highlands of Scotland, which are predominantly at amphibolite facies (from Morton et al., 2004). Note the predominance of Type B garnet (low Mg, variable Ca).

the Lesser Caucasus source region is dominated by basic volcanic rocks (Kazmin et al., 1986), and provides heavy mineral suites rich in clinopyroxene (Morton et al., 2003a). The association of Type D garnets with clinopyroxene-dominated assemblages suggests that they were derived from very low-grade metabasic rocks, similar to those found in New Zealand (Coombs et al., 1973). Dasgupta and Pal (2005) have indicated another possible origin for Type D garnets. They found that grandite garnets of variable composition occur in ultra-high temperature metamorphosed calc-silicate granulites as a result of a number of reactions involving, among other minerals, clinopyroxene, scapolite, plagioclase, wollastonite and calcite.

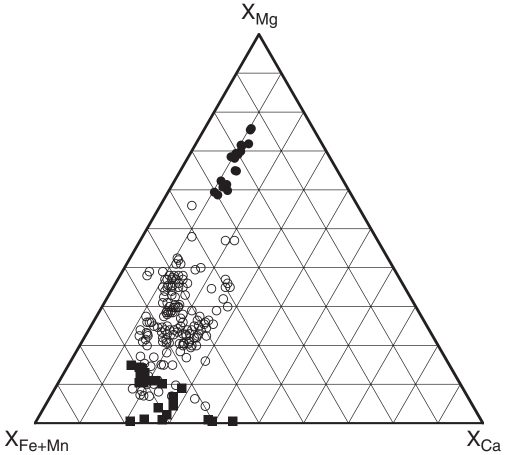


Fig. 4. Garnets in peridotites and pyroxenites (filled circles), in eclogites, other mafic gneisses, and quartz-biotite gneisses (open circles), and in granitic gneisses, tonalitic gneisses, hybridised gneisses and pegmatites (filled squares) from western Norway (Krogh, 1980; Medaris, 1980, 1984; Mysen and Heier, 1972). X_{Fe+Mn}, X_{Mg}, X_{Ca} are as in Fig. 1.

Although most detrital garnets have primary metamorphic sources, granitoids and associated pegmatites can also provide garnet-rich sediment. For example, garnet is common in the Dartmoor granite of SW England (Brammall, 1928) and in some Scottish granites (Mackie, 1926). Garnets from intermediate-acidic igneous rocks have distinctive low-Mg, low-Ca compositions and are frequently rich in Mn (Deer et al., 1997). Detrital garnets with these characteristics have been found in Oligocene sandstones of Georgia (Fig. 1), and were derived from granites located in the Dzirhuli Massif. Such garnets are classified as Type B using the terminology of Morton et al. (2004), but have a markedly different origin to the Type B garnets in Scottish river sediments (Fig. 3), which were derived from amphibolite facies metasediments. Subdivision of Type B garnets into Bi (X_{Ca}<10%) and Bii (X_{Ca}>10%) may therefore prove useful in differentiating sediment derived from granitoids, which supply assemblages dominated by Mn-rich Bi garnets (Fig. 1), and sediment derived from metasediments, which tend to have a wider range of compositions within the overall Type B spectrum. Integration of heavy mineral and mineral-chemical data provides further constraints on the origin of such detrital garnets.

A variety of other garnet types are known from igneous and metamorphic sources, including yamatoite ($Mn_3V_2Si_3O_{12}$), kimzeyite ($Ca_3(Zr,Ti)_2(Al,Si)_3O_{12}$) and yttrogarnet ($Y_3Al_2Al_3O_{12}$). Despite acquisition of a large amount of detrital garnet geochemical data, however, such garnets have yet to be recorded as detrital phases. The only exception to this is the vanadian garnet goldmanite ($Ca_3V_2Si_3O_{12}$), which was identified in Palaeocene sandstones in the northern North Sea by Hallsworth et al. (1992). Some garnets, in particular those containing high proportions of the pyrope (Mg) end member, also have high Cr contents: these are of special importance in diamond exploration, because chrome-rich pyrope garnet and/or chromite are important minor phases in many mantle-derived peridotites which appear as xenolits in kimberlites (McClenaghan and Kjarsgaard, 2001; Nowicki et al., 2007, this volume).

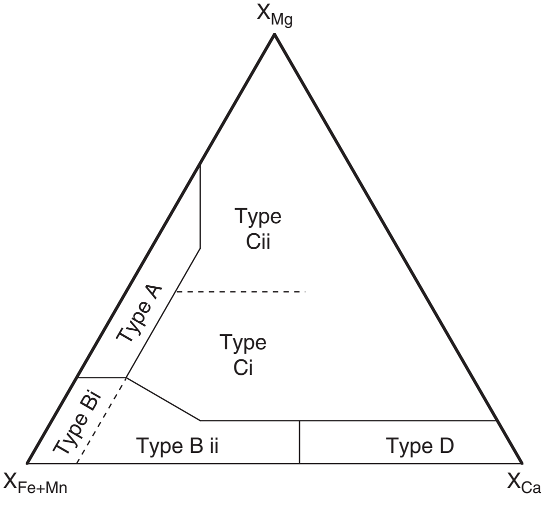


Fig. 5. Subdivision of the garnet Fe + Mn-Mg-Ca ternary plot showing definitions of garnet types A, Bi, Bii, Ci, Cii and D, as discussed in the text. Note that these types reflect natural sedimentary groupings, and are not intended to be diagnostic of particular garnet-bearing source rocks. Nevertheless, observations from modern and ancient sediments indicate the following: Type A garnets are mainly derived from high-grade granulite-facies metasediments or charnockites, but can also be supplied from intermediate-acidic igneous rocks sourced from deep in the crust. Type B garnets are derived from amphibolite-facies metasediments. However, garnet populations that plot exclusively in the Type Bi field suggest derivation from intermediate-acidic igneous rocks. Type C garnets are derived mainly from high-grade metabasic rocks. Within this group, garnets with very high Mg contents (Type Cii) imply sourcing from ultramafics such as pyroxenites and peridotites. Type D garnets are generally derived from metasomatic rocks such as skarns, from very low-grade metabasic rocks, or from ultra-high temperature metamorphosed calc-silicate granulites.

The vast majority of garnet geochemical studies have concentrated on major elements variations, which are readily determined using conventional electron microprobe methods. However, Čopjaková et al. (2005) combined major electron analysis using the electron microprobe with trace element analysis using laser ablation ICP-MS to provide additional insight into garnet provenance in the Culm Basin of the Czech Republic. They showed that trace element patterns are useful for distinguishing garnets from different granulite sources. For example, garnets derived from the Miroslav Crystalline Unit (Fig. 6) show strong enrichment in heavy rare earth elements (HREE), whereas those derived from the Náměšt' Granulite Massif have flat to negatively sloped chondrite-normalized HREE patterns. Although conventional electron microprobe methods are likely to remain at the forefront of detrital garnet studies, trace element analysis using laser ablation ICP-MS is likely to add significant sophistication to garnet provenance studies in the future.

Garnet geochemistry was used as a potential archaeometric tool by Mannerstrand and Lundqvist (2003) who traced the possible source rocks for the garnets found in the Slöinge excavation site in southwest Sweden and in Denmark to understand better Iron Age trade. Using SEM equipped with an EDS-detector they carried out

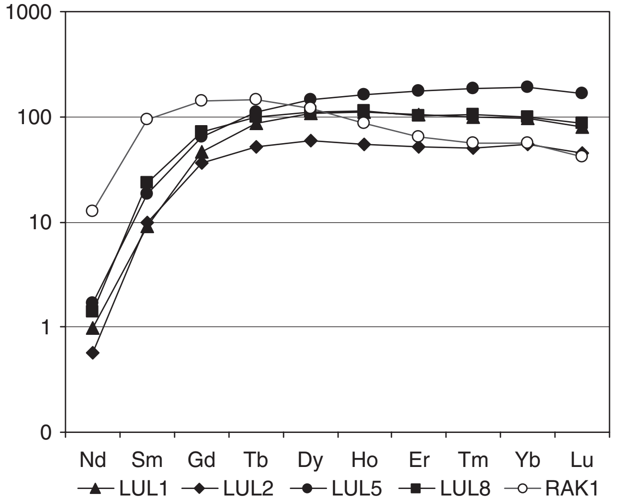


Fig. 6. Chondrite-normalised REE patterns of garnets derived from the Miroslav Crystalline Unit (samples LUL1, LUL2, LUL5 and LUL8) and the Náměšt' Granulite Massif (sample RAK1), from Čopjaková et al. (2005). Normalisation values from Taylor and McLennan (1985).

comparative analyses on garnets from potential source rocks in Sweden and their results indicated that the probable source rocks are garnet amphibolites/mafic granulites, common in southwest Sweden, and that an important trade with garnet from a few mines occurred during the late Iron Age.

The use of garnet geochemical data to solve questions concerning sediment provenance is limited by the stability of garnet during burial diagenesis. Although garnet is relatively stable during burial, it undergoes dissolution by high-temperature pore-fluids (Morton, 1984; Morton and Hallsworth, 2007, this volume). Furthermore, the stability of garnet is controlled by its composition, with high-Ca garnets being less stable than low-Ca garnets (Morton, 1987; Smale and Van der Lingen, 1989; Morton and Hallsworth, 2007, this volume). Therefore, Type Bii, Type C and Type D garnets are less stable than Type A and Type Bi garnets. In consequence, sandstones that have undergone significant modification during burial diagenesis may contain garnet assemblages that are not entirely representative of their source region. Garnet populations that have been modified by dissolution during deep burial can be recognised by petrographic observation of their surface textures (see Turner and Morton, 2007, this volume).

3.2. Chrome Spinel

Chrome spinel [$(Mg,Fe^{2+})(Cr,Al,Fe^{3+})_2O_4$] is a ubiquitous accessory mineral in ultramafic to mafic rocks. It owes its value as a petrogenetic indicator to its particular chemical character, being extremely sensitive to bulk rock composition and petrogenesis of the host rock. The principal constituents (Cr, Mg and Al) behave differently during fractional crystallisation or partial melting: Cr and Mg are strongly partitioned into the solid, whereas Al is strongly partitioned into the melt. Partitioning of Mg and Fe^{2+} between spinel, silicate melts and minerals is strongly temperature dependent (Irvine, 1965, 1967; Dick and Bullen, 1984; Hisada and Arai, 1993). The ratios of these cations change according to physicochemical conditions and equilibrium temperature, and can thus reveal petrogenetic signatures of geodynamic settings in which chrome spinel-bearing complexes are formed.

An extensive literature exists on the paragenesis, crystal chemistry and geotectonic significance of chrome spinel in mafic and ultramafic bodies, predominantly ophiolites, meta-ophiolites and other types of ultramafic bodies. Irvine (1965, 1967) was one of the earliest to recognise the value of chrome spinel as a petrogenetic indicator. His publications raised much interest, prompting researchers to unravel the geochemical properties of chrome spinels in a variety of geological environments. Studies aimed to reconstruct the petrogenesis and plate tectonic settings of igneous complexes and sediments sourced from them, and the proliferation of publications has greatly enriched the geological literature. For example, Dick and Bullen (1984) refined the discrimination field and provided a comprehensive review of chrome spinel as a petrogenetic indicator in abyssal and alpine-type peridotites, while Barnes and Roeder (2001) collated a wide spectrum of spinel compositional fields from a variety of mafic and ultramafic igneous rock types and their tectonic environment. Arai (1992) showed that the composition of chrome spinel in volcanic rocks is a reliable guide to magma chemistry.

For graphical evaluation, cation ratios are calculated as $Cr\# = Cr/(Cr + Al)$ and $Mg\# = Mg/(Mg + Fe^{2+})$, and plotted as bivariate plots (Dick and Bullen, 1984; Pober and Faupl, 1988; Arai, 1992; Sciunnach and Garzanti, 1997; Barnes and Roeder, 2001). Chrome spinels derived from different ophiolite parageneses cluster in distinctive areas in these plots (Fig. 7). Other bivariate diagrams are constructed by using TiO_2 wt% versus Fe^{2+}/Mg (Gansslose (1999), TiO_2 wt% versus $Cr/(Cr + Al)$ (Hisada et al., 1999) (Fig. 8), and/or other ratio combinations (Figs. 9 and 10). Ternary plots (Fig. 11) are constructed by plotting the major trivalent cations Cr^{3+}, Al^{3+} and Fe^{3+} (Cookenboo et al., 1997; Barnes and Roeder, 2001). They illustrate the fields delineating different types of ophiolites and other ultramafics.

The potential of detrital chrome spinel in fingerprinting sediment provenance and in reconstructing source rock composition and geotectonic setting has been demonstrated by numerous studies. Zimmerle (1984) was the first to recognise the geotectonic significance of "detrital brown spinel" (commonly referred to as chrome spinel), not only because its composition is a sensitive indicator of the parental melt but, also, because in detrital sediments its higher abundance correlates with orogenic episodes (e.g., Caledonian, Variscan and Alpine). He showed that a marked increase of "detrital brown spinel" in a succession marks the stratigraphical interval which records the beginning of processes that expose and progressively erode obducted ophiolitic mafic–ultramafic complexes. Evidence for such processes was demonstrated by Dewey and Mange (1999) in the western Irish Caledonides. Press (1986) was one of the first to use chrome spinel chemistry to trace the source of Middle Devonian sediments of the Rhenish Massif to alpine-type peridotites, and Pober and Faupl (1988) showed, in a comprehensive study, how chrome spinel chemistry helped understanding the geodynamic evolution of the eastern Alps. An increasing number of publications focus on chrome spinel chemistry, alone or combined with that of

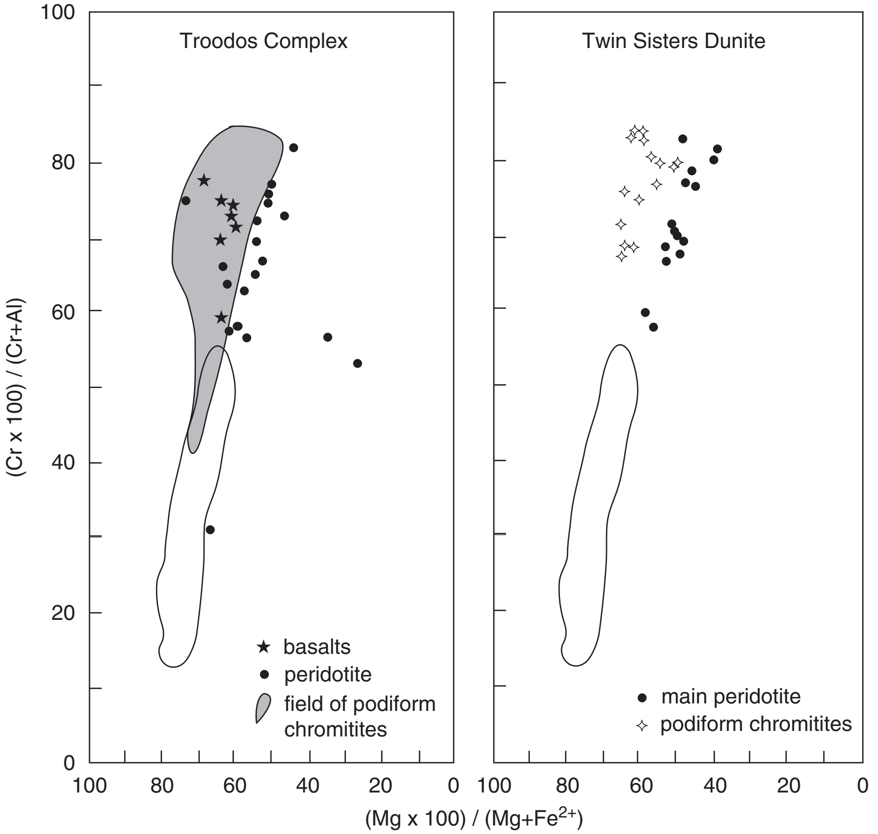


Fig. 7. Mg# versus Cr# bivariate plots, showing the compositional fields of chromian spinels for alpine-type peridotites. Solid circles are spinel peridotites, filled stars basalts, and open stars are chromitites or dunites (after Dick and Bullen, 1984).

other mineral phases present in the heavy mineral fractions. These include, amongst others, Arai and Okada (1991), Hisada and Arai (1993), Gieze et al. (1994), Árgyelán (1996), Arai et al. (1997, 2006), Cookenboo et al. (1997), Sciunnach and Garzanti (1997), Asiedu et al. (1998, 2000a), Hisada et al. (1998, 1999, 2004), Gansslosel (1999), Preston et al. (2002), Zhu et al. (2004), Mikes et al. (2005), Oszczypko and Salata (2005) and Grzebyk and Leszczyński (2006).

Lenaz and Kamenetsky (2000) were the first to analyse melt inclusions in detrital chromian spinels, extracted from Maastrichtian to Middle Eocene sandstones of sedimentary basins in the SE Alps. Based on their TiO_2 and Fe^{2+}/Fe^{3+} contents, they successfully discriminated two principal compositional groups which indicated one peridotite and one basaltic volcanics-sourced spinel population. Furthermore, heterogeneous geochemical characteristics within the latter group indicated that they were generated in different basaltic melts in different plate tectonic environments. Zhu et al. (2004) adopted this novel approach and included it in their study of the Middle-Late Cretaceous turbiditic sandstones of the Tianba Flysch series in southern Tibet.

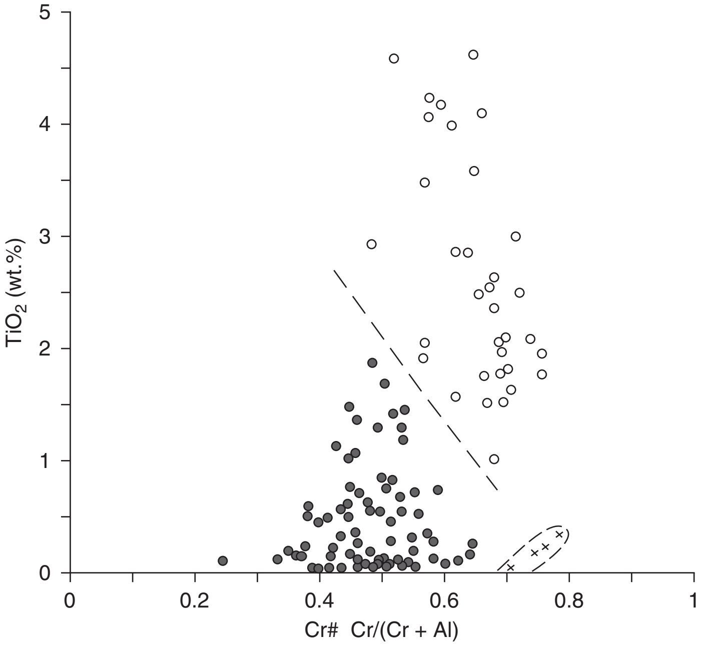


Fig. 8. Chrome spinel bivariate plot based on Cr# versus TiO2 wt%. Open circles show high-Ti spinels, solid circles low Ti spinels and crosses high-Cr spinels (after Hisada et al., 2004).

A brief review of the geotectonic significance of detrital chrome spinel was published by Lee (1999), however Power et al. (2000) challenged its validity as a petrogenetic indicator. The latter authors analysed the chemistry of chrome spinels from different parts of the Rum intrusion, a layered complex in the British Tertiary Volcanic Province, and from streams draining the Rum complex. They found that chrome spinels have diverse chemistry within individual megacyclic units and that disseminated detrital chrome spinels are chemically comparable but are different from the within-seam chrome spinels. Because the mechanism of formation and chemistry of parental magma of the within-seam chrome spinels are different to those of their disseminated counterparts, they generate chrome spinels with different chemistry. Power et al. (2000) argued that disseminated and within-seam spinels are, therefore, not equivalent, a finding that contrasts with Irvine's (1965, 1967) assumptions. Chrome spinels from stream samples were sourced from disseminated chrome spinels from the main body of the intrusion, rather than from chromitite seams, indicating that the latter contributed only minor amounts to the detritus. They also noted that hydrothermal alteration and serpentinisation causes changes in chrome spinel chemistry. During serpentinisation, chrome spinel grains lose Al and Mg and become enriched in Fe; this change particularly affects disseminated chrome spinels. They conclude that chrome spinels occur in much wider tectonic settings than the currently-used discrimination diagrams suggest. In this context, it is worthy of note that the Rum intrusion formed in a Palaeocene hotspot setting, different to that of other ultramafic complexes and oceanic lithosphere.

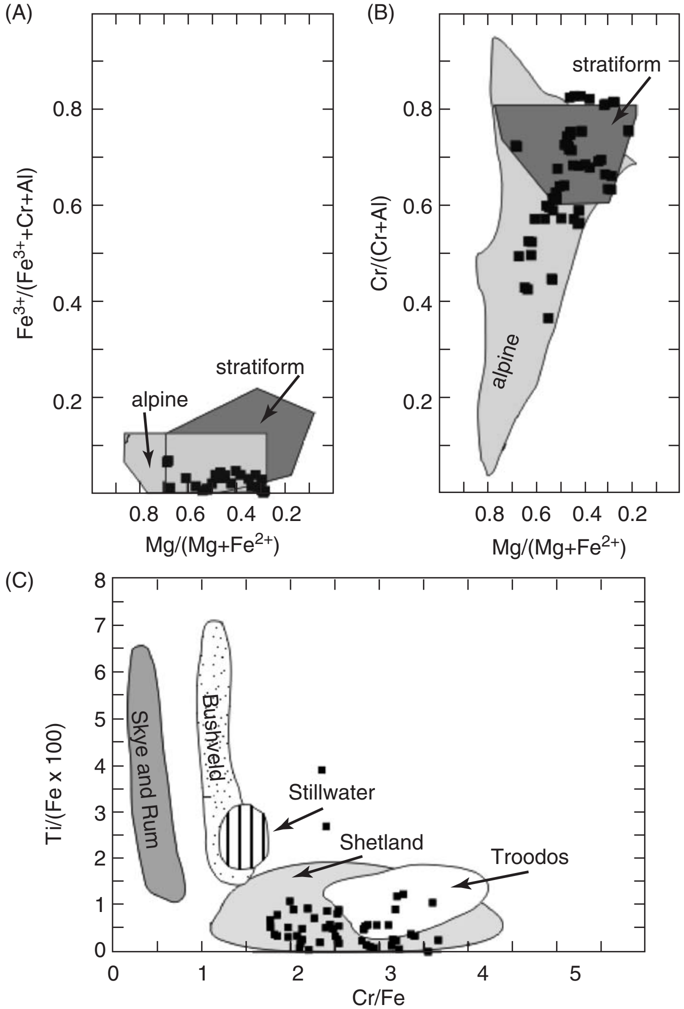


Fig. 9. Major-element composition of chrome spinels from Triassic red beds in the Beryl Field, North Sea, UK. (A) $Mg/(Mg + Fe^{2+})$ and $Fe^{3+}/(Fe^{3+} + Cr + Al)$ ratios are plotted from well 9/13-S48 and compared with chrome spinels from stratiform- and alpine-type ultramafic rocks (after Dick and Bullen, 1984; Cookenboo et al., 1997). (B) Major-element composition of chrome spinels from well 9/13-S48 plotted using $Mg/(Mg + Fe^{2+})$ and $Cr/(Cr + Al)$ ratios, which are compared with chrome spinels from stratiform- and alpine-type ultramafic rocks (after Dick and Bullen, 1984; Cookenboo et al., 1997). (C) Ti/Fe versus Cr/Fe ratio plot for chrome spinels from well 9/13-S48 compared with those from layered ultramafic intrusions (Skye, Rum, Bushveld and Stillwater), and with chrome spinels from ophiolitic sources (Shetland and Troodos) (after Prichard and Neary, 1985).

Detrital chrome spinel chemistry also serves as an important alluvial tracer for diamond in kimberlite terrains. This particular use is reported by Nowicki et al. (2007, this volume). Chrome spinel chemistry is a powerful tool in the evaluation of the ore quality in economic mineral deposits (Pownceby, 2005), and proved valuable

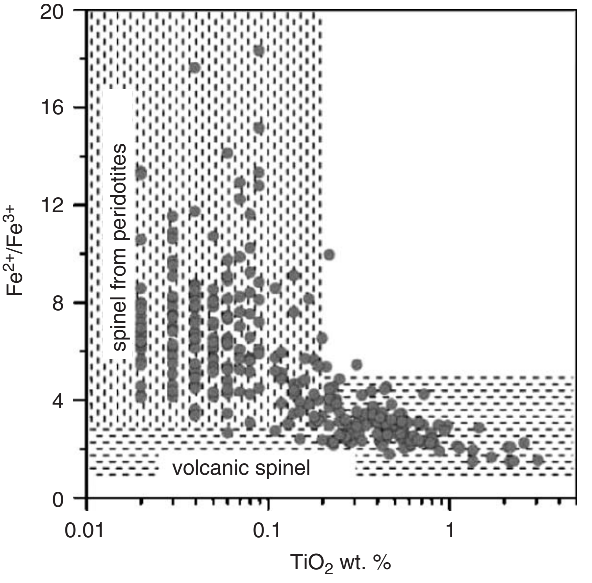


Fig. 10. Cross plot for discriminating volcanic and peridotite-derived chrome spinels, using TiO_2 wt% versus Fe^{2+}/Fe^{3+} (after Lenaz and Kamenetsky, 2000).

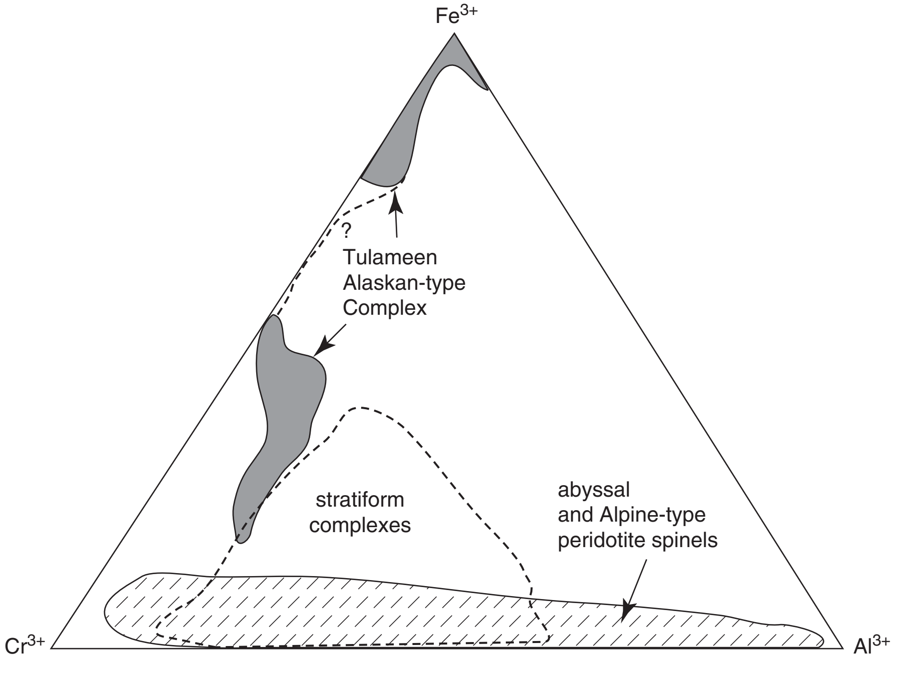


Fig. 11. Trivalent major cation plot, discriminating between different types of ultramafic complexes (after Cookenboo et al., 1997).

in solving a problem in commercially important Ti mineral deposits in southeastern Africa (Pownceby and Bourne, 2006). Because even minor Cr levels can downgrade the ilmenite concentrate, it was important to find the source of the Cr-bearing mineral phase. Chrome spinel analyses showed the presence of two distinctive compositional groups, denoting two chemically-different provenances. One group of spinels had a high magnetite component and these could be easily removed, thus increasing the value of the concentrates.

Chrome spinel is chemically more stable than all other minerals in ultramafic rocks, and preserves its compositional signature after burial. The minor disadvantage lies in the possibility of recycling, but this is generally negligible because most tectonogenic sediments are first cycle. If recycling is suspected, it can be easily ascertained by grain morphology and by the character of associated minerals. Chrome spinel is easily recognised both in transmitted light and reflected light petrography.

This review of studies using chrome spinel geochemistry is far from complete. However the examples cited above provide an insight into a repository of information to draw from, and to guide researchers in the field of sedimentology, tectonics and other disciplines.

3.3. *Tourmaline*

Tourmaline is a complex borosilicate with a considerable range of potential compositions. Its general formula is $XY_3(T_6O_{18})(BO_3)_3V_3W$ (Hawthorne and Henry, 1999). The X site may be occupied by Na, Ca or possibly K, but can be largely vacant. The Y site is usually occupied by Li^{1+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, V^{3+}, Fe^{3+} or Ti^{4+}. The T site is usually occupied by Si, occasionally Al, and possibly B. The V site contains OH^{1-} and O^{2-}, whereas the W site contains F^{1-}, OH^{1-} and O^{2-}. The wide range of potential compositions makes tourmaline an ideal mineral to use for geochemical discrimination of provenance. The application of tourmaline geochemistry in provenance studies has been enhanced by the work of Henry and Guidotti (1985) and Henry and Dutrow (1992), who demonstrated that tourmaline geochemistry reflects the local environment in which the mineral developed. They showed that the use of two ternary diagrams (Al-Fe_{total}-Mg and Ca-Fe_{total}-Mg) enabled discrimination of tourmalines from a wide range of rock types (Fig. 12). These provenance discrimination diagrams are very powerful, because they permit not only an evaluation of similarities and differences between detrital tourmaline populations, but they also put constraints on the nature of their source areas. Furthermore, because tourmaline is stable in both weathering and diagenetic environments (Morton and Hallsworth, 1999, 2007, this volume), tourmaline geochemistry can be applied to provenance analysis of any sandstone, irrespective of the extent to which it has been modified during the sedimentary cycle.

Despite the evident potential of tourmaline geochemistry for provenance analysis, the method has been applied only sporadically to date. Willner (1987) used the technique to evaluate the provenance of Precambrian/Cambrian sandstones in Argentina. Jeans et al. (1993) suggested that variations in tourmaline composition in the UK Triassic reflect differences in provenance. Tourmalines also proved useful to constrain the provenance of Early Jurassic sandstones in Slovakia (Aubrecht and

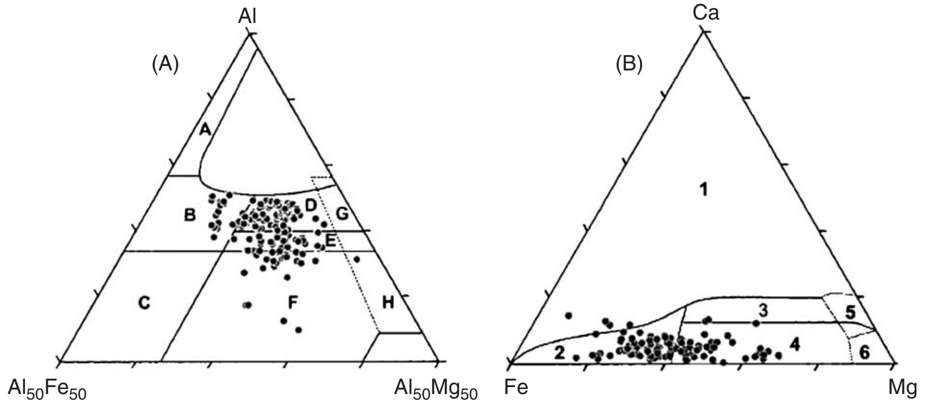


Fig. 12. Tourmalines from the Triassic of the Beryl Field, northern North Sea, plotted on the provenance-discriminant Al-Fe_{total}-Mg and Ca-Fe_{total}-Mg ternary diagrams of Henry and Guidotti (1985), adapted from Preston et al. (2002). Plot A: Field A, Li-rich granitoids, pegmatites and aplites. Field B, Li-poor granitoids, pegmatites and aplites. Field C, Hydrothermally-altered granitic rocks. Field D, Aluminous metapelites and metapsammites. Field E, Al-poor metapelites and metapsammites. Field F, Fe^{3+}-rich quartz-tourmaline rocks, calc-silicates and metapelites. Field G, Low-Ca ultramafics. Field H, Metacarbonates and metapyroxenites. Plot B: Field 1, Li-rich granitoids, pegmatites and aplites. Field 2, Li-poor granitoids, pegmatites and aplites. Field 3, Ca-rich metapelites, metapsammites and calc-silicates. Field 4, Ca-poor metapelites, metapsammites and quartz-tourmaline rocks. Field 5, Metacarbonates. Field 6, Metapyroxenites.

Kristin, 1995), of Jurassic to Cretaceous sandstones of Papua New Guinea (Morton et al., 2000), and of Triassic sandstones in the northern North Sea (Preston et al., 2002). Jiang et al. (1999) analysed tourmalines in clasts from Devonian conglomerates of SW Ireland, thereby establishing the nature of the metamorphic basement source and its affinity with other basement blocks in Ireland. Li et al. (2004) suggested that tourmaline compositions in Carboniferous sandstones of central China reflect an evolution in their source area with time. Morton et al. (2005a) showed that northerly- and southerly-derived Carboniferous sandstones of the southern North Sea contain different tourmaline geochemical populations, an observation that is particularly significant in view of the extensive diagenetic modification that has caused depletion of all but the most stable heavy minerals.

Tourmaline geochemistry proved to be a vital component of the multidisciplinary provenance study of Late Cretaceous sandstones in the Norwegian Sea (Morton et al., 2005b). Their study used a combination of heavy mineral data, provenance-sensitive ratio data, garnet geochemistry, tourmaline geochemistry and zircon geochronology to identify three main sources, each of which generated a distinctive sand type. Sand type MN1 was derived from northern Norway, sand type MN2 was derived from northern East Greenland and sand type MN3 was derived from western Norway. A total of 64 tourmaline populations were analysed during the course of this study, each of which was characterised by electron microprobe data from 50 individual tourmalines. The tourmaline populations consist mainly of metasedimentary types (falling in fields D, E and F on the Al-Fe_{total}-Mg ternary diagram as defined by Henry and Guidotti, 1985), with minor numbers of grains derived from Li-poor granitoids (Field B), as shown by the typical tourmaline populations in Fig. 13. The relative abundances of Field B, Field D, Field E and Field F tourmalines vary systematically between the three sand types (Fig. 14), enabling distinction of their provenance and placing constraints on the tourmaline-bearing lithologies in the source regions.

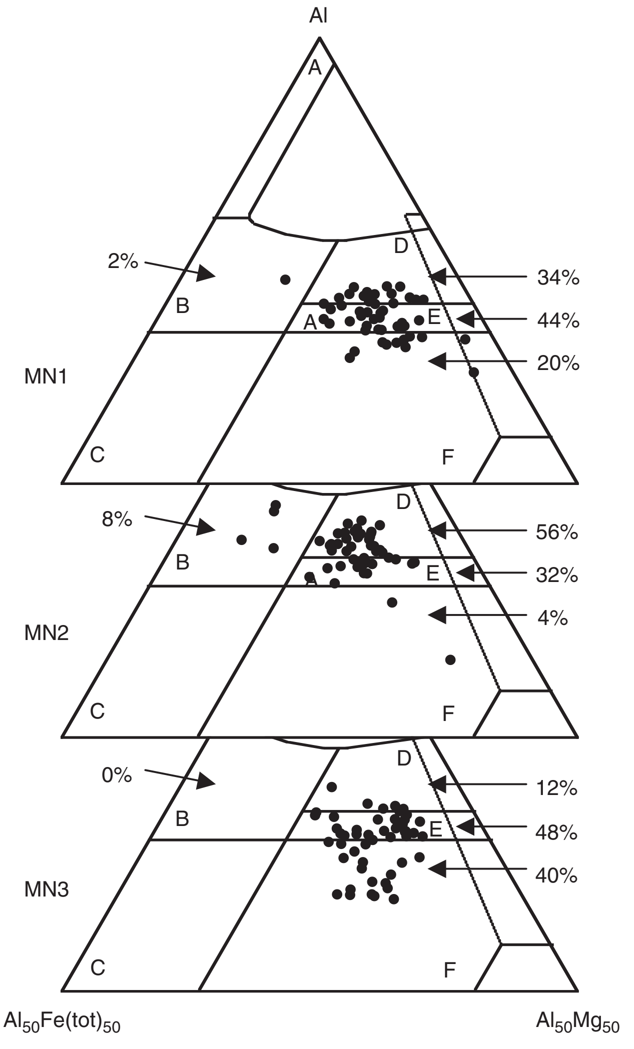


Fig. 13. Typical tourmaline assemblages from Late Cretaceous sandstone types MN1, MN2 and MN3 from the Norwegian Sea plotted on the provenance-discriminant Al-Fe_{total}-Mg ternary diagram devised by Henry and Guidotti (1985) (after Morton et al., 2005b). Figures denote percentage of grains falling into fields B, D, E and F. See Fig. 12 for definition of the fields illustrated. MN1, well 6507/2-2, depth 3338.5 m; MN2, well 6607/5-2, depth 4172.9 m; MN3, well 6305/7-1, depth 2959.0 m.

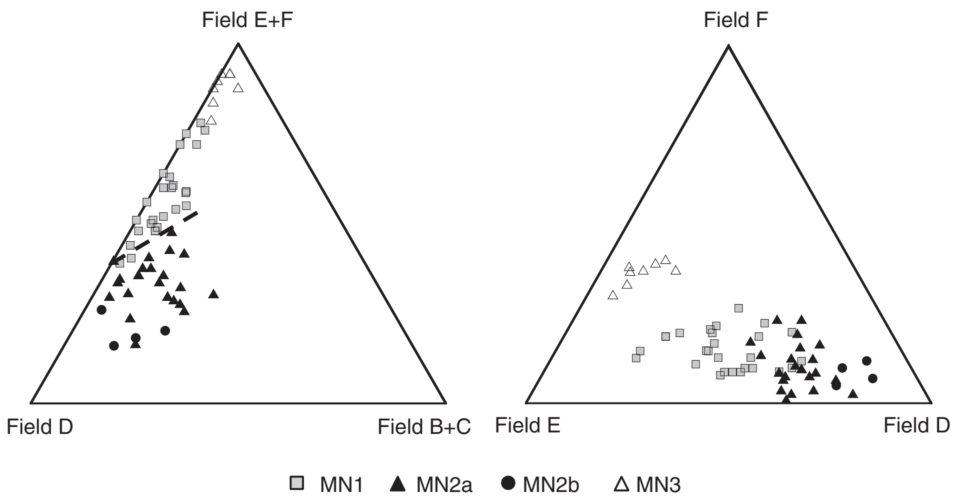


Fig. 14. Discrimination of provenance of Late Cretaceous sandstone types MN1, MN2 and MN3 from the Norwegian Sea using tourmaline geochemical data (from Morton et al., 2005b). Fields B, C, D, E and F as defined by Henry and Guidotti (1985).

3.4. Pyroxenes

Pyroxenes are the most important group of ferromagnesian rock-forming minerals. They occur in almost every type of igneous and metamorphic rocks, and crystallise under a range of different conditions (Deer et al., 1992). The pyroxene group includes orthorhombic [orthopyroxenes: (Mg,Fe)SiO_3] and monoclinic (clino) pyroxenes. The latter are members of the four-component system $CaMgSi_2O_6$-$CaFeSi_2O_6$-$Mg_3Si_2O_6$-$Fe_3Si_2O_6$.

Comprehensive studies of pyroxene compositions in sedimentary successions are considerably fewer than for garnet and chrome spinel, partly because of the unstable character of pyroxenes under weathering and diagenetic conditions. Chemical compositions of pyroxenes in their parent rocks are well-established for all parageneses, and this knowledge is an essential guide to the study of pyroxenes in derived sediments. General guides to pyroxene classification include the discrimination diagram of Poldervaart and Hess (1951) and the nomenclature of pyroxenes by Morimoto (1988). The work of Leterrier et al. (1982) on using clinopyroxene composition for the identification of palaeovolcanic magmatic affinities, and that of Nisbet and Pearce (1977) on clinopyroxene composition in mafic lavas from different tectonic settings are amongst the most frequently cited. Clinopyroxene data is traditionally plotted on the diagrams established by Poldervaart and Hess (1951), Nisbet and Pearce (1977) and Morimoto (1988). Important information is provided by Le Bas (1962) on the role of aluminium in igneous pyroxenes and their affinities to particular magma types.

Although many pyroxenes are removed from sediments by dissolution processes (weathering, diagenesis), they can be preserved in the sedimentary record. Geochemical analyses have highlighted their usefulness in the reconstruction of

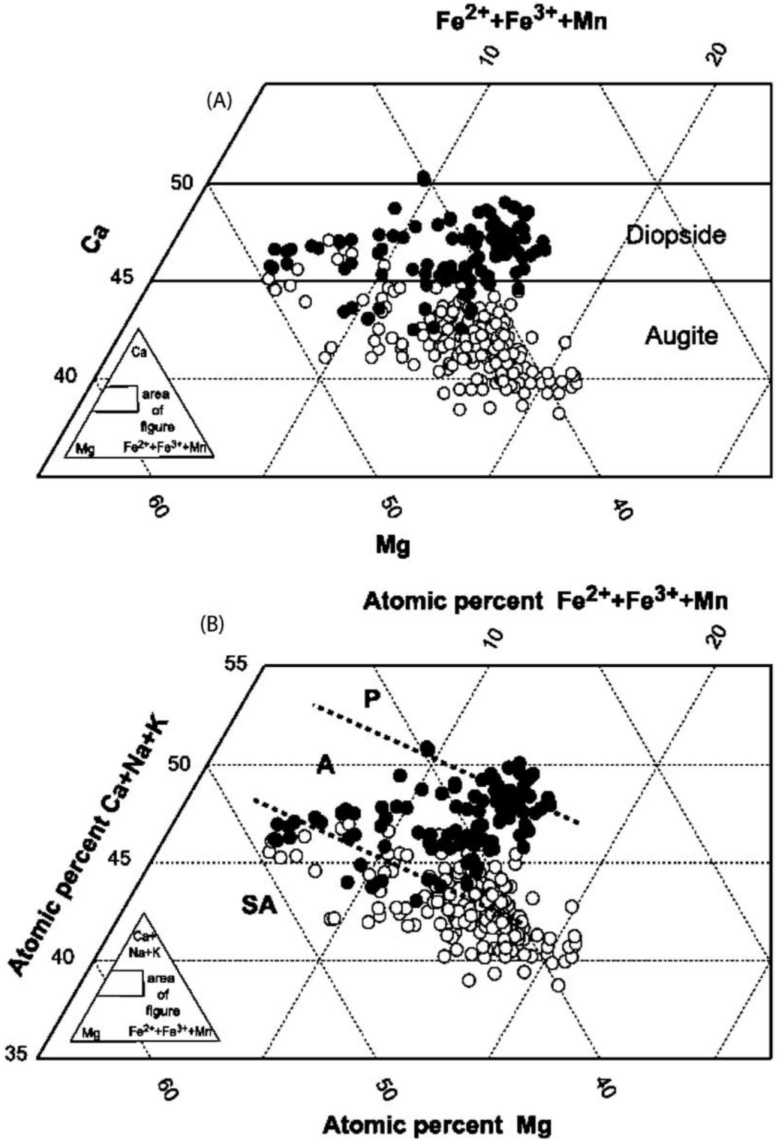


Fig. 15. Classification diagram for clinopyroxenes from sandstones in the Central Depression and Altiplano, Chile, using the scheme of Morimoto (1988). Open circles, Central Depression; filled circles, Altiplano (after Pinto et al., 2004). (A) Clinopyroxenes from the Central Depression (open circles) and Altiplano (filled circles). (B) Same data as in A, plotted on a discrimination diagram for subalkaline (SA), alkaline (A) and peralkaline (P) magma suites, using the discrimination scheme of Le Bas (1962).

geotectonic events, hinterland lithology and the provenance of the host sediment (e.g., Cawood, 1983, 1991a, b; Styles et al., 1989, 1995; Arai and Okada, 1991; Gieze et al., 1994; Acquafredda et al., 1997; Krawinkel et al., 1999; Lee and Lee, 2000; Pinto et al., 2004).

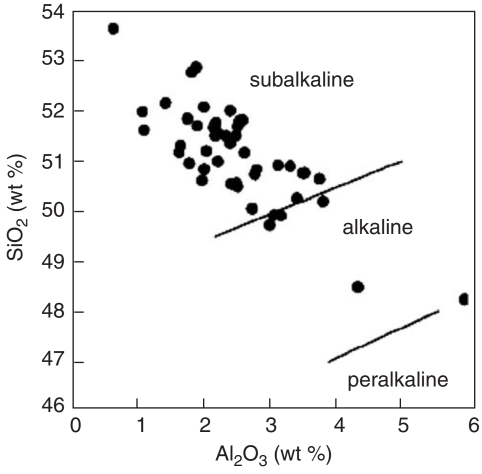


Fig. 16. Clinopyroxene compositions reflecting different tectonic settings. Plotting Al_2O_3 wt% against SiO_2 wt% enables clinopyroxenes from subalkaline, alkaline and peralkaline sources to be distinguished (after Lee and Lee, 2000).

Figs. 15 and 16 are examples of graphical presentations, drawn from publications by Pinto et al. (2004) and Lee and Lee (2000).

Determination of the crystal chemistry of pyroxenes is a fundamental part of the research on pyroxene-bearing rocks in a mosaic of plate boundary zones and in continental domains. Numerous publications provide templates for comparative work on pyroxenes in sedimentary basins. Cawood (1991a) shows a relevant example from the Tonga arc, where the geochemistry of pyroxenes in the volcaniclastic sediments furthered our understanding of the history of the New England Fold Belt complex in southeastern Australia. Cawood's petrographic and chemical analyses reveal that Miocene to Recent volcaniclastic sediments from the Tonga arc indicate derivation from a relatively uniform, low-K tholeiitic province. In the New England Fold Belt relict pyroxene compositions from the lower part of the stratigraphic pile suggest derivation from a transitional low-K to calc-alkaline source. By contrast volcaniclastic sediments deposited during the later stages of arc evolution indicate the emergence of a calc-alkaline to high-K tholeiite source.

Noda et al. (2004) integrated a range of methods, including sandstone petrography, modal analysis of conglomerate clasts and their major and trace element chemistry, chemical compositions of detrital pyroxene and garnet, and K-Ar geochronology to understand better the evolution of the Murihiku Terrane, New Zealand. This multi-method approach constrained its formation during the Middle Jurassic, while detrital clinopyroxene compositions indicated detritus from an island arc source.

Krawinkel et al. (1999) combined the techniques of sandstone petrography, heavy mineral analysis and clinopyroxene geochemistry of lithic sandstones in a comprehensive study of Middle Eocene to Late Neogene successions of the Azeuro-Soná Complex of NW Panama. The geochemistry of the pyroxenes enabled recognition of changing magma compositions of the clinopyroxene host rocks, thus adding further constraints to sediment provenance and to palaeogeographic and plate tectonic reconstructions.

A similarly detailed and informative work is that of Pinto et al. (2004) on Neogene basins in the Central Andes. Clinopyroxene chemistry indicates that the volcanic sources of the successions in the Mauri and Corque basins of the Bolivian Altiplano had different degrees of magmatic differentiation and alkalinity, whereas the pyroxene-bearing host rocks which supplied sediments to the Central Depression in Chile were less differentiated. Markevich et al. (2007, this volume) showed how pyroxene geochemistry can illuminate discrimination, provenance and dispersal of tectonogenic sediments in the dynamic regimes surrounding the western Pacific subduction complexes. Schneiderman (1997) analysed detrital clinopyroxenes from the Nile and its delta, and was able to differentiate between clinopyroxenes shed from the Ethiopian highlands and those sourced by the Red Sea Hills on the basis of their chemistry. Pyroxene suites from the latter were identified by the presence of diopside, titaniferous augite and orogenic, high Ca, low Cr + Ti augite.

3.5. Amphiboles

Amphiboles constitute an extremely complex group of minerals that form in a variety of igneous and metamorphic rocks. They crystallise over a broad spectrum of P-T conditions, with a wide variation of chemical and physical properties (Leake, 1978; Deer et al., 1992; Mange and Maurer, 1992; Leake et al., 1997). The strong relationship between these properties and the conditions of crystallisation is displayed, in a limited way, by their optical properties but can be identified precisely by their chemistry. For allocation of individual members of the amphibole group, data are plotted on the diagrams defined in the amphibole nomenclature of the Subcommittee of Amphiboles (Leake, 1978; Leake et al., 1997). Preceding this nomenclature sodic amphibole analyses were plotted on the Miyashiro diagram (Miyashiro, 1957).

Members of the amphibole group are well represented in young detrital sediments and, being more stable than pyroxenes, are more frequently encountered in older strata. However, by contrast with pyroxenes, relatively few studies include a systematic, sequential analysis of the geochemistry of sedimentary amphiboles, especially calcic amphiboles. The standard optical practice relies on distinguishing orthorhombic amphiboles, the generally fibrous grains of the tremolite-ferroactinolite series, other amphiboles and, within the hornblende group colour varieties, such as green-brown, blue-green and deep-brown oxy-hornblende. More interest is paid to sodic amphiboles (blue amphiboles of the glaucophane-riebeckite series) because their paragenesis indicates high-pressure/low-temperature origin and exhumed subduction complexes.

The chemistry of detrital amphiboles from Palaeogene sediments in the southwest Rockall Plateau area (located south of Iceland and west of the British Isles) was determined by electron microprobe analysis by Morton (1991). These analyses permitted the differentiation of two distinct amphibole suites, associated with contrasting heavy mineral assemblages, signalling different source provinces. One suite that contains actinolite, actinolitic-hornblende and magnesio-hornblende, and is associated with epidote group minerals, including piemontite, points to a Greenland

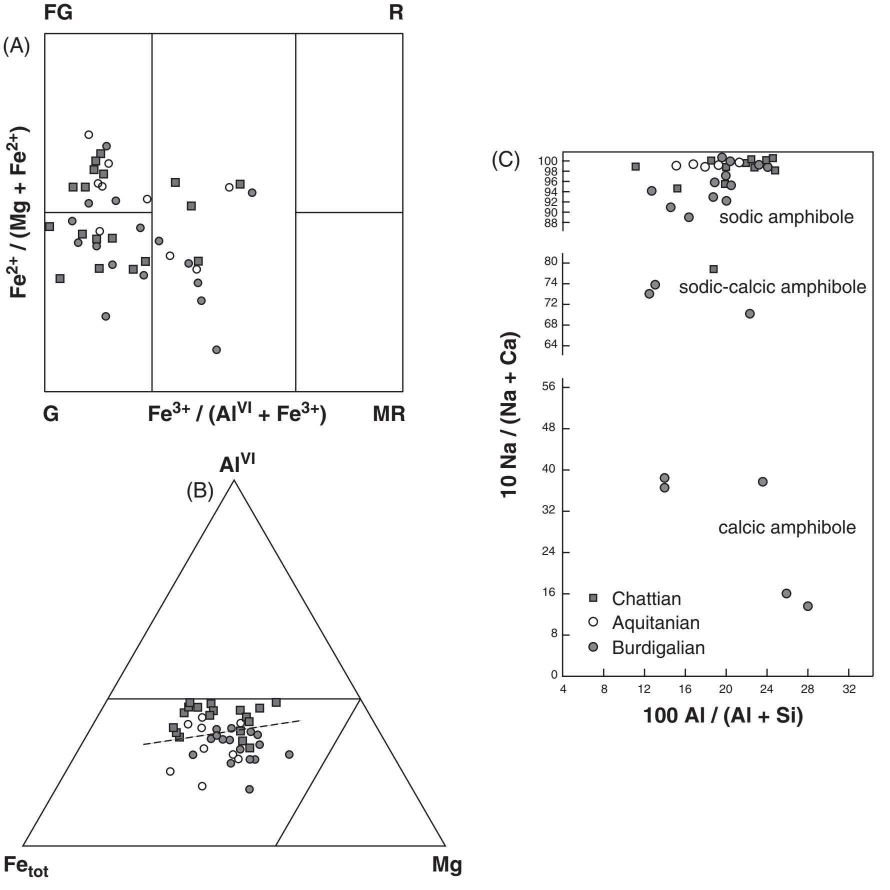


Fig. 17. Blue sodic amphibole, sodic-calcic amphibole and calcic amphibole compositions from the peri-Alpine Molasse Basin of France. Chattian blue amphiboles have dominantly glaucophane and ferroglaucophane compositions whereas Burdigalian amphiboles show sodic-calcic and calcic amphibole compositions (after Mange-Rajetzky and Oberhänsli, 1982). (A) Blue sodic amphibole compositions plotted on the Miyashiro diagram (FG = ferroglacophane, R = riebeckite, G = glaucophane, MR = magnesio-riebeckite). (B) Ternary plot showing the separation of blue sodic amphiboles from the Chattian and Burdigalian molasse. (C) Bivariate plot showing the age-related spread of blue sodic amphibole, sodic-calcic and calcic amphibole compositions.

provenance. The other suite contains an edenite and pargasite suite, and is found in association with clinopyroxene, garnet and apatite. Differences in geographical distribution suggest that the former suite was derived from southern Greenland, whereas the latter originated on the Rockall Plateau.

Schäfer (1996) and Schäfer et al. (1997) studied a large number of detrital amphiboles from Palaeozoic greywackes from the Erbendorf, Saxothuringian flysch, Germany. Integrated with other methods, their aim was to constrain exhumation at a Variscan active margin. The amphiboles, identified as magnesio- and tschermakitic hornblende, had a remarkably similar composition throughout. By comparing them

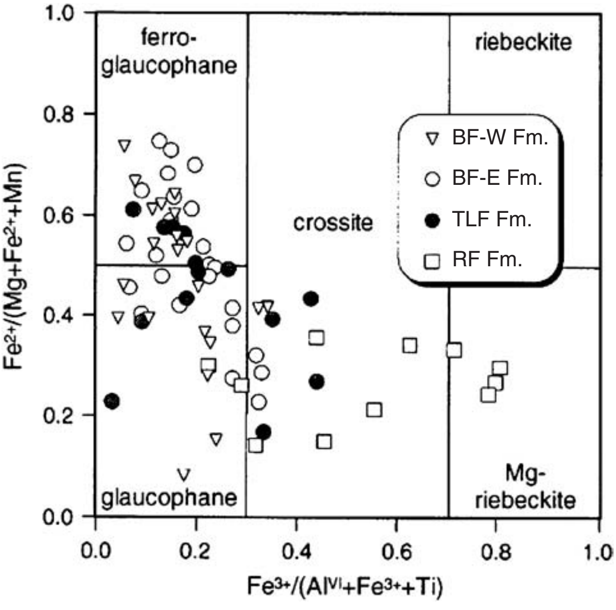


Fig. 18. Blue sodic amphiboles from Cretaceous synorogenic sandstones in the Eastern Alps plotted on the classification diagram of Leake (1978) (from Von Eynatten and Gaupp, 1999). BF-W, Branderfleck West Fm.; BF-E, Branderfleck East Fm.; TLF, Tannheim and Losenstein Fms; RF, Rossfeld Fm.

with amphiboles from neighbouring mafic rocks, they found a good correspondence with amphibolites of the Münchberg klippe to the northwest. These results were compatible with data achieved by other comparative geochemical methods (Schäfer, 1996).

Von Eynatten and Gaupp (1999), in a comprehensive study of the provenance of Cretaceous synorogenic successions in the Eastern Alps, determined the composition of several heavy mineral species, including green and brown calcic amphiboles whose chemistry reveals the presence of several members of the hornblende series and varying compositions within the tremolite-ferroactinolite series. Linking these amphibole suites to specific parent rocks greatly increased the resolution of provenance reconstruction. Durn et al. (2007, this volume; their Fig. 13) analysed calcic amphiboles from terra rossa in Istria, Croatia, to identify the different detrital input during terra rossa formation. Calcic amphibole chemistry also proved useful in geoarchaeology and helped to trace the source of temper in Roman ceramics (Freestone and Middleton, 1987).

Knowledge of the geotectonic evolution of the Hellenides is considerably augmented by studies of the detrital components of various tectonic units. Detrital blue sodic amphibole geochemistry from Palaeocene flysch in the western Othrys Mountain, Pelagonian Zone s.l. (Faupl et al., 2002), revealed that they were chemically comparable with blue amphiboles from the Cyclades. Their occurrence is consistent with the Cretaceous onset of blueschist facies metamorphism in parts of the Hellenides, especially in the Cycladic belt. Further details on the tectonic units of the Hellenides are provided by Faupl et al. (2007, this volume).

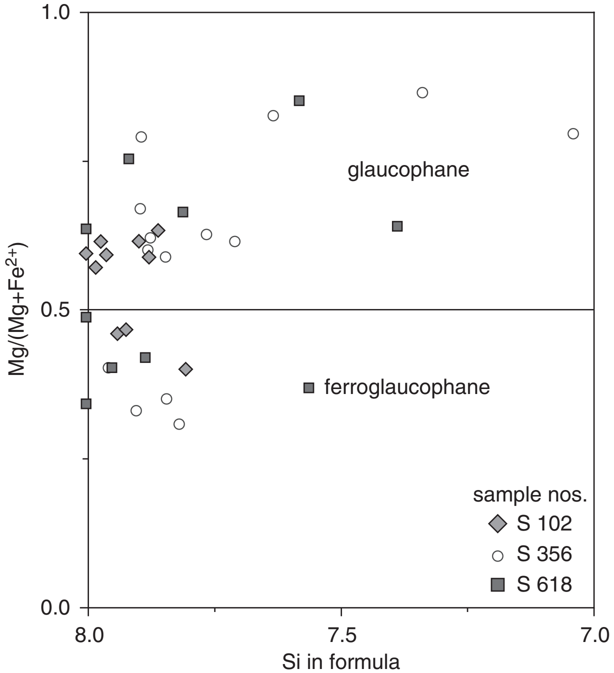


Fig. 19. Blue sodic amphibole compositions from the Ordovician Portpatrick Formation, Southern Uplands, Scotland, plotted on the classification diagram of Leake et al. (1997) (after Mange et al., 2005).

Acquafredda et al. (1997) analysed blue amphiboles from the southern Apennines, Ganssloser et al. (1996) from greywackes of the Harz Mountains and Mange-Rajetzky (1981) from southern Turkey. Mange-Rajetzky and Oberhänsli (1982) studied the chemistry of blue sodic amphiboles in the Peri-Alpine molasse, France. Systematic compositional changes of the blue amphiboles in successive Oligocene/Miocene lithostratigraphic units mirrored the exhumation and erosional unroofing of the products of different phases of high-pressure, low-temperature metamorphism in the Alpine internal zone. Al-rich glaucophane and ferro-glaucophane in Early Chattian sediments were formed during the eo-Alpine high-pressure phase, whereas Ca-bearing and Mg-rich crossite and glaucophane from the Burdigalian molasse were generated at a later stage, associated with more diverse metamorphic conditions. Changes in calcic amphibole compositions paralleled the trend of sodic amphiboles (Fig. 17).

Von Eynatten and Gaupp (1999) included analysis of blue sodic amphiboles from various stratigraphic units in their study of the Cretaceous sandstones in the Eastern Alps. Plots, using the classification scheme of Leake (1978), reveal the presence of a heterogeneous blue amphibole population (Fig. 18). Glaucophane, ferroglaucophane and crossite were well-represented and magnesio-riebeckite was also identified. The results shed new light on the exhumation of high-pressure rocks in the hinterland during, at least, Albian to Coniacian time. Von Eynatten and Gaupp (1999) also concluded that blue amphiboles from the oldest formation were probably derived from different lithologies.

Amphibole geochemistry provided significant new data to the still imperfectly solved provenance of the Southern Uplands Terrane, Scotland (Mange et al., 2005). Blue amphiboles of glaucophane and ferroglaucophane composition, and newly discovered lawsonite in the Portpatrick Formation, defined blueschist derivation (Fig. 10 in Mange et al., 2005) (Fig. 19). Associated garnet in the same formation contains inclusions with sodic-calcic amphibole composition, prompting the authors to invoke a cryptic terrane for the provenance of these enigmatic detritus. The most likely source is Avalonia, which probably incorporated a Cadomian fragment, before collision with Laurentia.

3.6. Apatite

The value of apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, as a provenance indicator has been relatively underplayed, for a variety of reasons. Firstly, apatite is a common accessory mineral in virtually all igneous and many metamorphic rocks (McConnell, 1973; Nash, 1984; Chang et al., 1998), and is therefore not an especially specific provenance indicator mineral. Secondly, its distribution in sandstones is commonly controlled by the extent of weathering during the sedimentary cycle, rather than provenance (Morton and Hallsworth, 1999). Thirdly, apatite shows only limited major element geochemical variations (Chang et al., 1998), confined to substitution of F (fluorapatite), Cl (chlorapatite) and OH (hydroxyapatite). This effectively precludes the use of conventional electron microprobe analysis in the acquisition of provenance-sensitive data. Consequently, until recently, the only varietal studies of apatite have dealt with its morphological properties. For instance, apatite morphology has proved useful as a tool for reservoir subdivision and correlation in Triassic sediments of the Irish Sea (Mange et al., 1999) and in Devonian to Carboniferous sandstones from the Clair oilfield, west of Shetland (Allen and Mange-Rajetzky, 1992; Morton et al., 2003b).

The recent advent of LA-ICPMS has enabled accurate determination of trace element abundances on single apatite grains. This has opened a new dimension to mineral-chemical provenance studies, because trace element abundances in apatite are known to be controlled by the composition of the host rock.

Several elements, such as Sr, Y, Mn, U, Th and the rare earth elements (REE), substitute for Ca in igneous apatite, usually in trace amounts (Nash, 1984; Ayers and Watson, 1993; Chang et al., 1998; Belousova et al., 2002b). Trace element abundances appear to be related to whole rock SiO_2 contents, indicating that the degree of host rock fractionation is a major control on apatite compositions in igneous rocks. For example, Y, Mn and the heavy rare earth elements (HREE) become relatively enriched during fractionation, whereas Sr becomes relatively depleted. Belousova et al. (2002b) proposed that apatite host rocks can be discriminated using binary plots of abundances of elements such as Sr-Y and Sr-Mn. The Th contents are also lower in highly fractionated rocks, possibly due to crystallisation of monazite, which removes Th and the light rare earth elements (LREE) from the melt (Belousova et al., 2002b). By contrast, U is more abundant in granites and granite pegmatites than in dolerites (Belousova et al., 2002b). Dill

(1994) suggested that the Th-U binary plot is a useful diagram for discrimination of provenance, and this may be partly due to the different behaviour of the two elements during fractionation.

The total REE abundances in apatite are controlled by the REE content of the host rock, the greatest REE contents being found in apatites from alkaline rocks (Chang et al., 1998; Belousova et al., 2002b). The shape of the chondrite-normalised REE pattern is also controlled by the host rock composition (Nash, 1984), in particular the degree of fractionation (Belousova et al., 2002b). Apatites from less-fractionated mafic rocks have strong relative LREE enrichment, whereas those from highly fractionated rocks, such as granite pegmatites, show relative LREE depletion. Belousova et al. (2002b) therefore proposed that $(Ce/Yb)_{cn}$ (where 'cn' denotes 'chondrite-normalised') is a useful index of host rock composition. Fleischer and Altschuler (1986) came to a similar conclusion, although they proposed the use of a different parameter $[(La+Ce+Pr)/\Sigma REE]$. Fleischer and Altschuler (1986) also showed that the gradient shown by the LREE is a useful discriminant of apatites from silicic and alkaline magmas. For example, apatites from granites and granite pegmatites have low La/Nd ratios, whereas those from alkaline rocks (including pegmatites) have high La/Nd ratios.

Many apatites have negative Eu anomalies on chondrite-normalised REE plots, being especially pronounced in more fractionated rocks. According to Budzinski and Tischendorf (1989), this is probably caused by feldspar crystallisation, which concentrates Eu^{2+} from the melt. Thus, Belousova et al. (2002b) propose that the magnitude of the Eu anomaly (Eu/Eu*) is another useful measure of host rock composition.

In two case studies investigating the application of apatite geochemistry in provenance studies, Morton and Yaxley (2007) show that the most useful discriminators of apatite provenance appear to be the $La/Nd - (La+Ce)/\Sigma REE$ plot proposed by Fleischer and Altschuler (1986) and the Th-U plot proposed by Dill (1994). The examples considered by Morton and Yaxley (2007) concern Pliocene sandstones of the South Caspian Basin and Devonian to Carboniferous sandstones of the Clair Oilfield, west of the Shetland Islands (off Scotland).

During the Pliocene, two major river systems, the palaeo-Kura and the palaeo-Volga, transported sediment into the western part of the South Caspian Basin (Baturin, 1947; Reynolds et al., 1998; Morton et al., 2003a). The palaeo-Kura drained the Lesser Caucasus mountain belt to the west, which mainly comprises mafic igneous (largely volcanic) rocks of both low-Ti (calc-alkaline) and high-Ti (alkaline) compositions, ophiolites and metamorphic rocks (Kazmin et al., 1986). The palaeo-Volga system had a much larger catchment area on the Russian Platform to the north, largely comprising Phanerozoic sediments that form the cover of the East European Craton, together with basement rocks, many of gneissic nature.

The apatite populations (Fig. 20) faithfully reflect the differences in lithology between these two source regions. The majority of palaeo-Kura apatites have moderate to high La/Nd and high $(La+Ce)/\Sigma REE$ ratios, falling in the fields defined by mafic/intermediate and alkaline host rocks, consistent with the widespread distribution of basic volcanic rocks of both alkaline and calc-alkaline compositions in the Lesser Caucasus. By contrast, the palaeo-Volga apatite populations include a large number of grains derived from silicic sources, characterised by low La/Nd and

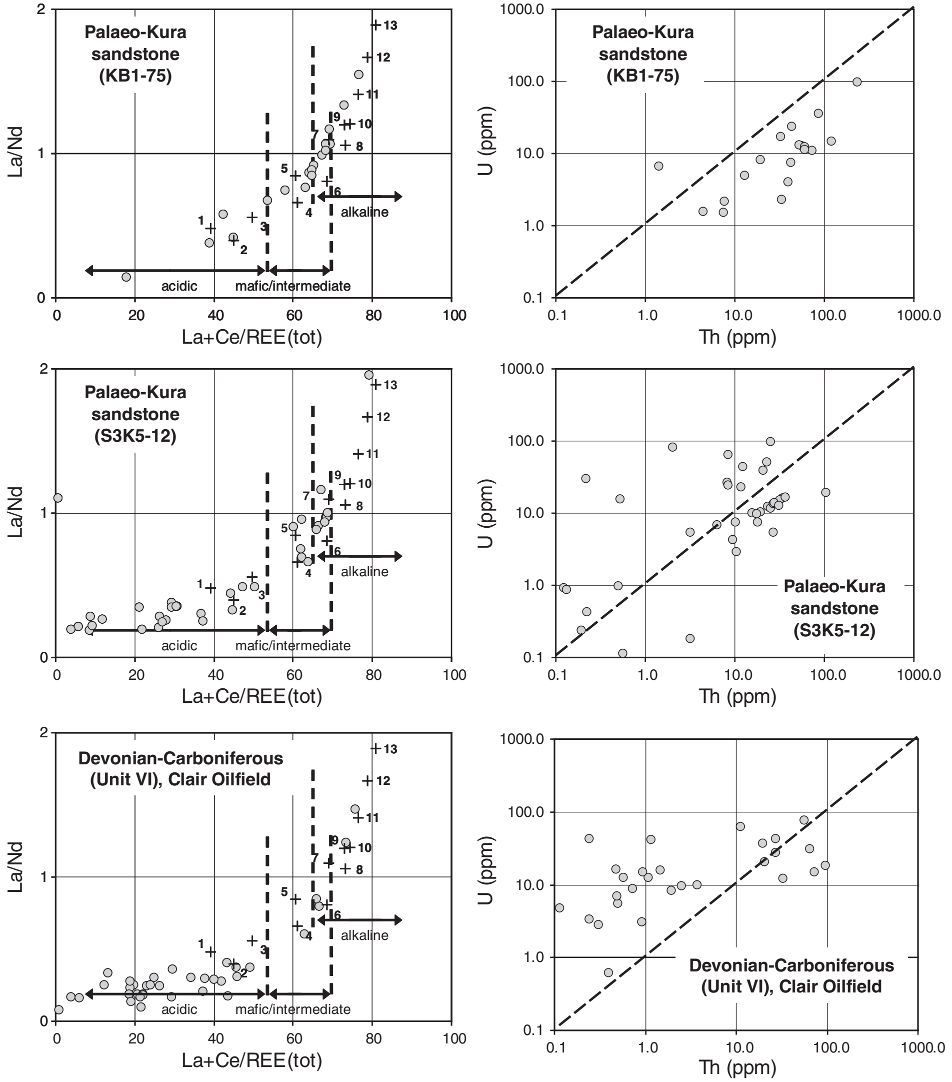


Fig. 20. Representative apatite populations in Pliocene sandstones of the South Caspian Basin and Devonian-Carboniferous sandstones of the Clair Oilfield plotted on the La/Nd – (La + Ce)/ΣREE classification diagram of Fleischer and Altschuler (1986) and the Th-U plot of Dill (1994), adapted from Morton and Yaxley (2007). 1, granite pegmatite; 2, gneiss/migmatite; 3, granite; 4, gabbro; 5, granodiorite; 6, kimberlite; 7, syenite; 8, alkali ultramafic; 9, carbonatite; 10, iron ores; 11, ultramafic; 12, alkaline; 13, alkaline pegmatite.

low (La + Ce)/ΣREE ratios. Apatites derived from alkaline host rocks (high La/Nd, high (La + Ce)/ΣREE ratios) are especially scarce in the palaeo-Volga sandstones. Virtually all the palaeo-Kura apatites have Th > U, consistent with the scarcity of highly-evolved rocks, such as granitoids, in the Lesser Caucasus. By contrast, approximately 40–60% of the palaeo-Volga apatites have $Th < U$, indicating the widespread occurrence of acidic rocks, consistent with the evidence from the La/Nd – (La + Ce)/ΣREE plot. The greater diversity shown by the palaeo-Volga apatite populations reflects the larger size of the catchment area and the polycyclic nature of the sediment, which would inevitably have introduced sediment from a wide range of sources. The large number of apatites derived from highly evolved rocks indicates that the ultimate source of the palaeo-Volga sediment contained widespread granites and/or acidic gneisses, a typical feature of ancient cratonic basement terrains. The geochemistry of both the palaeo-Kura and the palaeo-Volga apatite populations contrasts markedly with that of the Devonian/Carboniferous sandstones from the Clair Oilfield. The great majority of Clair Field apatites have low La/Nd and low (La + Ce)/ΣREE ratios, thereby falling in the acidic field on the La/Nd – (La + Ce)/ΣREE plot (Fig. 20), with subsidiary intermediate/mafic apatites and very few of alkaline composition. Most of the apatites in Clair Field sandstones have $U > Th$ (Fig. 20). These features combine to indicate that the source regions supplying sediment to the Clair Oilfield area during the Devonian and Carboniferous contained wide tracts of rocks with highly evolved (silicic) compositions.

Allen and Mange-Rajetzky (1992) and Nichols (2005) considered that Archaean gneisses of the Lewisian Complex (Hebridean Craton, Scotland) formed an important part of the source area for the Devonian to Carboniferous succession of the Clair Oilfield. The gneisses of the Lewisian Complex are predominantly tonalitic, trondhjemitic or granodioritic in composition, with subordinate granite gneiss sheets and lenses (Park et al., 2002). The apatite geochemical data are therefore consistent with derivation from Lewisian gneisses. However, it is also possible that the apatites were recycled from sediments ultimately derived from the Lewisian Complex, such as those forming the Proterozoic metasedimentary successions of northern Scotland (the Moine and Dalradian). These metasediments are also considered to be a potential source for the Clair succession (Allen and Mange-Rajetzky, 1992), and some contain a large amount of Archaean detritus (Cawood et al., 2003). It is also possible that younger (Proterozoic) basement complexes may also have been involved, either directly or indirectly.

Dill (1994), Belousova et al. (2002a) and Morton and Yaxley (2007) demonstrate that apatite geochemical data acquired by LA-ICPMS have considerable potential value for provenance reconstruction. The stability of apatite during deep burial (Morton and Hallsworth, 2007, this volume) makes the method applicable to diagenetically-modified sediment, which is a limiting factor for the large number of minerals that are unstable in the subsurface (notably pyroxene, amphibole and epidote). However, apatite is unstable under acid weathering conditions, and thus the method will be difficult to apply to sandstones that have undergone prolonged weathering during transport. The possible modification of the compositional range of apatite populations during weathering, by selective removal of the more unstable apatite varieties, may also be a factor. At present, unequivocal identification of provenance using apatite geochemistry is limited by the lack of a comprehensive database on apatite compositions in some of the potential source rocks, particularly those of metamorphic origin. Further work is therefore needed in order to improve the identification of prospective apatite source lithologies.

4. HEAVY MINERALS USED INFREQUENTLY FOR GEOCHEMICAL ANALYSIS

4.1. Chloritoid

Chloritoid [$(Fe^{2+},Mg,Mn)_2(Al,Fe^{3+})(OH)_4Al_3O_2(SiO_4)_2$] is an index mineral in two metamorphic parageneses, reflected in its crystal chemistry. It is most common in low-to-medium-grade metapelites which have a high Al and Fe content but occurs also in metasediments and metabasalts with ophiolitic affinities and in pelitic blueschists. Al-Fe chloritoid with additional Mn is characteristic of regionally-metamorphosed metapelites, whereas chloritoid appears in high-pressure rocks with a high Mg content (Chopin and Schreyer, 1983; Goffé and Bousquet, 1997). Such distinctive geochemistry implies that detrital chloritoid is a diagnostic provenance indicator. However, few heavy mineral studies include studies of chloritoid composition. Morton (1991) showed that chloritoids in the Early Jurassic Bridport Sands of Dorset, UK, have similar compositions to those from metapelites in the Ile de Groix in France, supporting the concept of a southerly source for these sediments (Davies, 1969). Nanayama (1997) included a small number of chloritoid analyses in a provenance study of Amazon fan sediments. Von Eynatten and Gaupp (1999), in their study of Cretaceous sandstones in the eastern Alps, used chloritoid geochemistry to infer derivation from blueschist facies rocks, and Lonergan and Mange-Rajetzky (1994) obtained evidence for the exhumation of the deepest part of the Internal Zone of the Betic Cordillera, Spain, from the appearance of high-Mg chloritoid in Langhian sediments (Fig. 21).

4.2. Epidote Group

Epidote minerals crystallise dominantly in regionally-metamorphosed rocks but also form in a wide variety of igneous parageneses, and they are also common in the sedimentary record. Compositionally they include zoisite and clinozoisite [$Ca_2Al_2O \cdot AlOH \cdot [Si_2O_7][SiO_4]$], epidote [$Ca_2Al_2O\ (Al,Fe^{3+})OH[Si_2O_7][SiO_4]$], piemontite [$Ca_2(Mn^{3+},Fe^{3+},Al)_3O \cdot OH[Si_2O_7][SiO_4]$] and allanite [$Ca,Mn,Ce,La,Y)_2$-$Fe^{2+},Fe^{3+},Ti)Al,\ Fe^{3+})_2O \cdot OH[Si_2O_7][SiO_4]$].

Because of their occurrence in a broad range of lithologies, they are not typically diagnostic of provenance. The stability of epidote minerals under burial diagenesis is higher than that of calcic amphiboles, andalusite and sillimanite but lower than that of titanite (Morton and Hallsworth, 2007, this volume).

Reports on the chemistry of epidote minerals in sediments appear only in few publications. Yokoyama et al. (1990) analysed epidotes from Neogene sediments of the Bengal fan, and detected limited compositional variations on the basis of $Fe^{3+}/(Al+Fe^{3+})$ ratios. However, they identified two distinctive zones, one characterised by the presence of zoisite, and another with a narrow range in $Fe^{3+}/(Al+Fe^{3+})$ ratios. These variations were ascribed to heterogeneity in the predominantly Himalayan source and to subordinate supply from the Indian subcontinent. Gieze et al. (1994) found that epidotes in Ordovician greywackes in the Rügen borehole on the Island of Rügen, Germany, have homogeneous compositions. Asiedu et al. (2000b) showed that epidotes in the Early Cretaceous Sasayama Group sandstones of SW

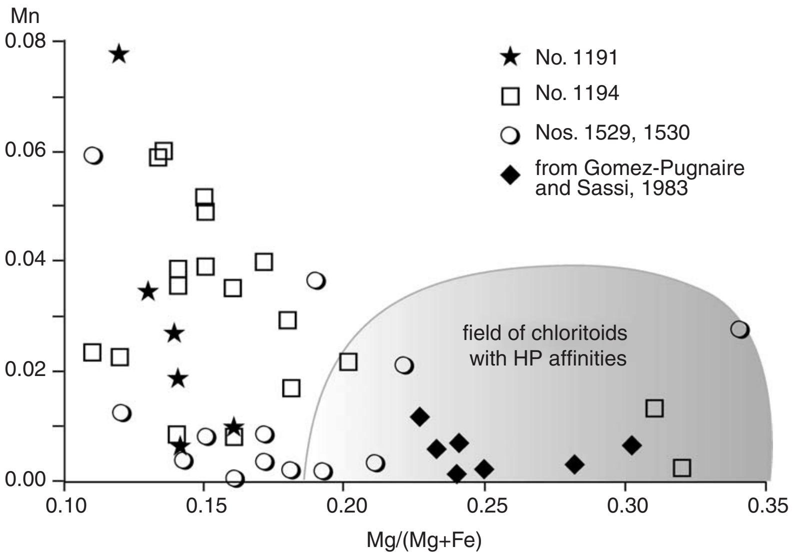


Fig. 21. Bivariate plot showing changing chloritoid compositions with the progressive exhumation of the internal zone of the Betic Cordillera, Spain. High-Mg chloritoids in the Burdigalian sandstones signal the exhumation of high-pressure rocks (after Lonergan and Mange-Rajetzky, 1994). Y axis shows ionic proportions on the basis of 14 O,OH. No. 1191, No. 1194, Nos. 1529, 1530 are sample numbers.

Japan have wide $Fe^{3+}/(Al+Fe^{3+})$ ratios and linked these to greenschist to epidote-amphibolite facies metamorphic rocks. Durn et al. (2007, this volume) analysed epidote group minerals from terra rossa on the island of Korčula (approximately 300 km SE of Istria, Croatia). These epidotes fall in a relatively narrow compositional range, with $Fe^{3+}/(Al+Fe^{3+})$ ratios ranging from 0.239 to 0.157, suggesting low-grade metamorphic source complexes.

Although traditional microprobe analyses yield informative data for the chemical characterisation of epidote minerals, tracing epidote assemblages to their potential parent rocks has limitations. Epidotes with similar compositions appear in a wide spectrum of rock types, and so may be delivered from geologically different source regions. When such sediments become intermixed, for example, in large fluvial systems or on continental shelves, they lose their provenance identity. This problem was addressed in a study of detrital epidotes from sandstones of the Swiss molasse basin by Spiegel et al. (2002), which integrated isotopic and trace element compositions of epidotes with zircon fission track data. This approach therefore combined information from zircon, which is generally sourced from silicic parentages, and from epidote, which is more common in basic lithologies that are difficult to date because they are generally poor in zircon and white mica. The study used Nd and Sr isotopic data to differentiate between different types of epidote-bearing source parageneses, and in particular to find out whether they were eroded from crust- or mantle-derived rocks. Spiegel et al. (2002) proved that crustal and mantle source rocks could be clearly distinguished by Nd and Sr data of detrital epidote grains, which permitted the refinement of the exhumation history of the Oligo/Miocene Central Alps.

4.3. Staurolite

Staurolite $\{(Fe^{2+},Mg,Zn)_2(Al,Fe^{3+},Ti)_9O_6[(Si,Al)O_4]_4(O,OH)_2\}$ normally forms in Al-rich metapelites, but can occur also in metasediments of other compositions, such as metapsammites, under suitable conditions (Hoschek, 1967; Wallace, 1975; Deer et al., 1997). Kepezhinskas and Koryluk (1973) noted that there are variations in staurolite composition related to changing metamorphic environments, expressed by the ratio $(Fe^{2+}+Mn+Fe^{3+})/(Fe^{2+}+Mn+Fe^{3+}+Mg)$, which they termed 'ferruginosity'. Despite the evidence for compositional variations in staurolite related to metamorphic grade, detrital staurolite geochemistry has been rarely applied to provenance analysis. Morton (1991) reported regional and stratigraphic variations in staurolite chemistry, both in terms of Fe/Mg ratio and Zn contents, in North Sea sediments, reflecting changes in provenance. Nanayama (1997) included a small number of staurolite analyses in a provenance study of Amazon fan sediments. Acquafredda et al. (1997) analysed staurolite compositions in Plio/Pleistocene sediments of the southern Apennines, and showed that their compositions were comparable to those in their presumed source rocks.

4.4. Rutile

Rutile (TiO_2) is one of the ultrastable minerals and commonly occurs both in ancient and young sediments. In hard rocks it is widely distributed as an accessory mineral in magmatic and metamorphic parageneses. Zack et al. (2002) used electron microprobe and laser ablation microprobe data for a range of high-field strength and other trace elements in rutile from eclogites and garnet-mica schists from the Central Alps with the view of developing a useful provenance tracer. Their results indicate that trace element contents of detrital rutile grains have the potential to be used as a powerful tool for sedimentary provenance studies because they reflect the key element ratios (especially Nb/TiO_2 and Cr/TiO_2) of their source rocks. This may help to distinguish between sources of high-grade metamorphics, eclogites and high-pressure granulites from hydrothermal ore deposits and kimberlites.

In a follow-up study, Zack et al. (2004) discussed the use of rutile chemistry in quantitative provenance studies. Since rutile is one of the most stable detrital mineral, extracting geochemical information from it is of great importance, especially in the study of mature sediments that have been depleted in more diagnostic but less stable minerals. Zack et al. (2004) showed that input from the two principal sources of rutile (metapelites and metabasites) can be distinguished on the basis of their Nb and Cr contents. They also showed that Zr in metapelitic rutile, where it coexists with zircon and quartz, is extremely temperature dependent, indicating that the Zr content can be used to measure maximum metamorphic temperatures. This single-grain geothermometer is believed to be the first of its kind to be used in provenance studies.

Rutile compositions were analysed from hydrocarbon reservoirs in Triassic continental red-beds in the Beryl Field, North Sea, by Preston et al. (1998).

Combined with the geochemistry of garnet, chrome spinel and trace element data, they aimed at developing a method for subdividing and correlating biostratigraphically barren successions by geochemical fingerprinting. Detrital rutile compositions in the study well (Well 19/13a-S48) showed a considerable homogeneity (Fig. 22) being almost pure TiO_2 with only a small proportion containing appreciable Nb_2O_5 or FeO. The common presence of Nb-rich and Nb-poor rutiles in a single assemblage indicates that these grains are independent of size and/or hydraulic controls.

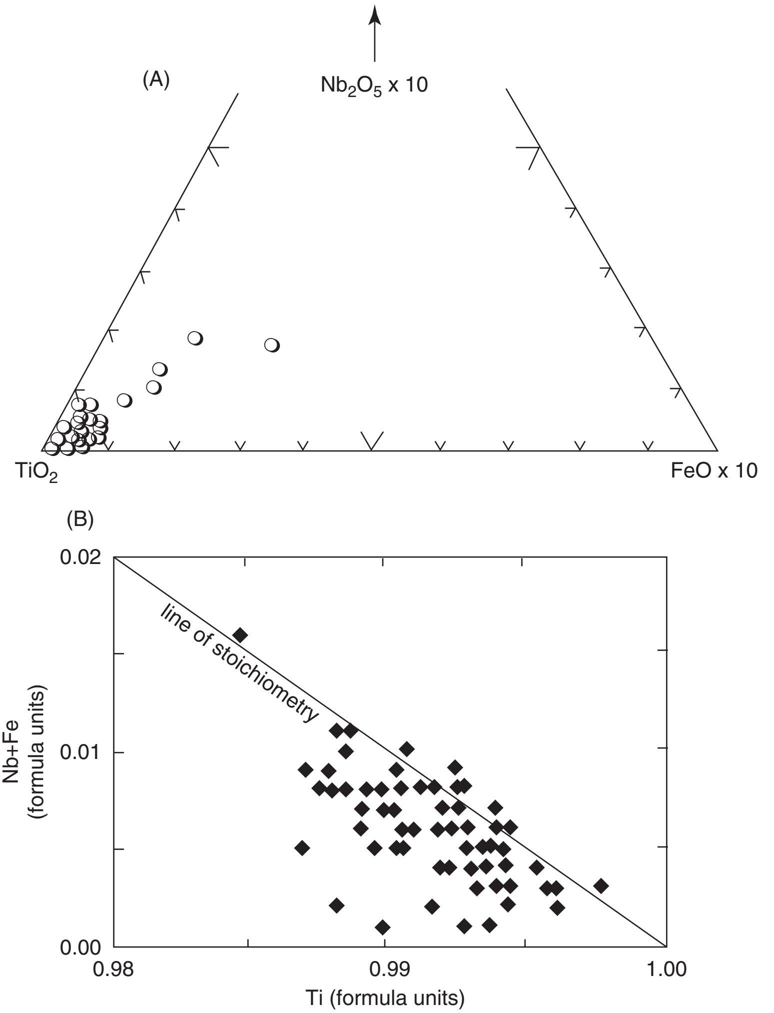


Fig. 22. Detrital rutile compositions from the Triassic red beds of the Beryl Field, North Sea, UK. (A) The majority of rutile grains fall into the almost pure TiO_2 field but a small portion shows higher Nb_2O_5 or FeO content. (B) Nb-poor rutile plotted along the line of stoichiometry, defined by the substitution scheme $3Ti^{4+} \rightleftharpoons 2NbO^{5+} + Fe^{2+}$. Deviation from this line indicates the presence of very small amounts of other trace elements such as Cr or Al (after Preston et al., 1998).

4.5. Monazite

Monazite [(Ce, Ld, Nd, Th)PO_4] occurs in silicic igneous rocks and in regionally metamorphosed argillaceous sediments (Overstreet, 1967; Nash, 1984; Chang et al., 1998), and compositional variations are reported to be related to paragenesis. Monazite crystals typically contain distinct compositional domains, many in the order of 5–10 μm, representing successive generations of mineral growth, which record details of the geological history of its host rocks. The electron microprobe can be used to characterise the geometry and quantitative composition of domains. In igneous rocks, the degree of LREE enrichment is related to host rock composition, with alkaline igneous rocks and carbonatites having much higher La/Nd ratios than granites and granite pegmatites (Fleischer and Altschuler, 1969). In metapelites, the ThO_2 content is generally related to metamorphic grade, the lowest values found in greenschist facies rocks, increasing through amphibolite facies, with the highest values found in the granulite facies (Overstreet, 1967). There may also be a relationship between temperature and Y content in monazite, with Y_2O_3 forming as much as 5% of high temperature monazites (Jonasson et al., 1988). However, these general observations are not always upheld: for instance, there is no relationship between metamorphic grade and Th content in metapelites of the eastern Mojave Desert, USA (Kingsbury et al., 1993).

Despite the evidence for variations in composition related to paragenesis, there have been remarkably few studies that relate detrital monazite composition to provenance. The obvious exception to this is the use of Th, U and Pb contents to date both detrital and secondary monazite in sediments using the CHIME (chemical Th-U-total Pb) method (e.g., Suzuki et al., 1991; Kusiak et al., 2006, and papers cited therein). However, geochronological methods (CHIME, together with conventional and microbeam U-Pb dating of monazite) are beyond the scope of this review.

4.6. Zircon

Zircon ($ZrSiO_4$) forms in a wide variety of igneous and metamorphic rocks, although it is most abundant in silicic igneous rocks such as granitoids. In provenance analysis, studies that concentrate on zircon almost exclusively concern single-grain U-Pb dating using techniques such as the SHRIMP or the LA-ICPMS. This geochronological approach is beyond the scope of this review: for further information, the reader is referred to Fedo et al. (2003). However, zircon displays variations in trace element contents that are believed to reflect host rock composition (Heaman et al., 1990; Hoskin and Ireland, 2000; Belousova et al., 2002a), and such variations have potential applications in provenance studies. The most significant variations are believed to be with the REE, but other trace elements such as U, Th, Y, Nb, Ta and Sc are also believed to have discriminatory potential. Owen (1987) proposed that Hf contents in detrital zircons could be used to discriminate provenance.

Heaman et al. (1990), in a study based on a relatively small data set, provided evidence that zircons from a variety of host rocks could be distinguished on the basis of Lu, Sc, Th/U, Lu/Sm and Hf. Belousova et al. (2002a) proposed that the total REE content increases from ultramafic, through mafic, to silicic whole rock compositions. In addition, there are variations in the REE patterns: zircons from carbonatites and kimberlites have relatively flat chondrite-normalised REE patterns, whereas those from granites and pegmatites show strong LREE depletion. A similar relationship was observed by Hoskin and Ireland (2000), who showed that mantle-derived and crust-derived zircons have different REE contents and patterns. However, their work suggested that it is not possible to discriminate between zircons from different crustal rock types. Metamorphic zircons can be distinguished from those of igneous origin on the basis of Th/U ratios, since magmatic zircons have Th/U ratios between 0.2 and 1.5, much higher than in metamorphic rocks, where the Th/U ratio is in the range 0.001–0.1 (Vavra et al., 1999; Hartmann et al., 2000). In a study of detrital zircons sourced from the Brazilian Shield, however, Hartmann and Santos (2004) showed that zircons from metamorphic sources are strongly under-represented, a fact that they attributed to preferential loss through abrasion during transport. For a detailed review of the composition of zircon in igneous and metamorphic rocks, the reader is referred to Hoskin and Schaltegger (2003).

In a provenance study of Carboniferous sandstones in the Pennine Basin, UK, Hallsworth et al. (2000) observed that zircons in the westerly-derived Clifton Rock had significantly lower U and Th contents than sandstones shed from the south (Dalton Rock, Halesowen Formation) or from the north (Rough Rock, Ashover Grit and pre-Marsdenian sandstone), as shown in Fig. 23. Zircons with high U and Th contents are more liable to become metamict (i.e., to have their crystal structure compromised), since they suffer a higher radiation dose through the emission of α particles (Holland and Gottfried, 1955). Metamict zircons are much more liable to dissolution during weathering compared with non-metamict grains (Balan et al., 2001), and are also more likely to be mechanically unstable. Hallsworth et al. (2000) suggested that the low U and Th contents in the Clifton Rock resulted from a polycyclic history, with repeated episodes of weathering and transport, leading to loss of zircons with high U and Th contents. The possible relationship between zircon composition and sediment maturity is a topic worthy of further investigation.

4.7. Ilmenite

Ilmenite ($FeTiO_3$) has long been the focus of geochemical analyses because it is one of the most important constituents of economic heavy mineral deposits (Pownceby, 2005; Pownceby and Bourne, 2006; Pirkle et al., 2007, this volume, and references therein). The chemistry of ilmenite and its trace element compositions for decoding petrogenetic signatures and provenance fingerprinting have been tested by Darby (1984), Darby and Tsang (1987), Grigsby (1991) and Asiedu et al. (2000a). Basu and Molinaroli (1991) found that ilmenite grains with TiO_2 contents between 50 and 60 wt% are more prevalent in metamorphic rocks, but they also occur in igneous rocks ranging in between 40 and 50 wt%. Schneiderman (1995) noted that ilmenite from metamorphic sources is richer in TiO_2 than ilmenite in igneous rocks. She also used detrital pyroxenes and ilmenite as provenance and palaeoclimate indicators in Nile delta deposits.

Schroeder et al. (2002) carried out a detailed investigation of the phases of ilmenite weathering in weathering profiles on granite and ultramafic chlorite schist for evidence of morphological and chemical alteration. Ilmenite grains in the schist

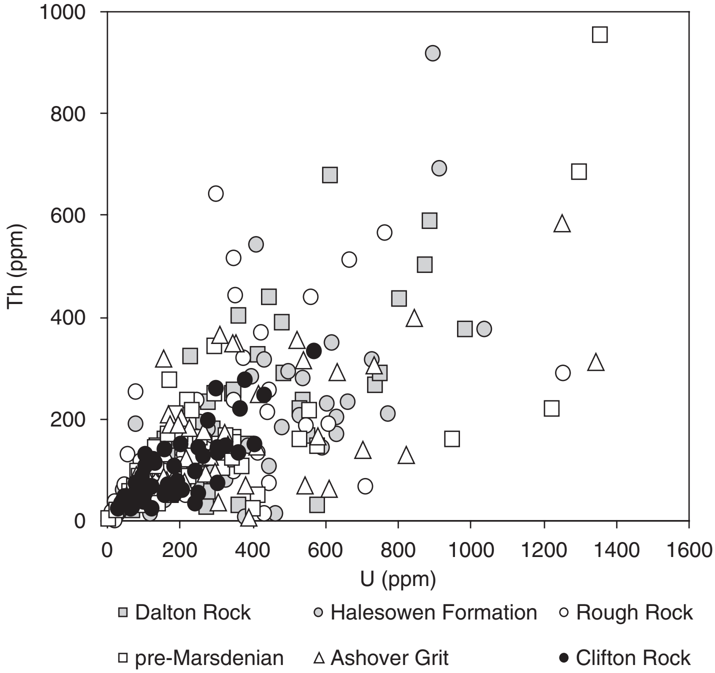


Fig. 23. U and Th contents of detrital zircons from Carboniferous sandstones of the Pennine Basin, UK (from Hallsworth et al., 2000).

profile occur as fractured anhedral grains with uncommon lamellae of rutile. Ilmenite from the granite profile is rich in Mn, which was also reported by Grigsby (1991) and Asiedu et al. (2000a). Ilmenite from the schist profile contained minor amounts of Mn. They recognised the development of two distinct grain populations, characteristic for each profile, and concluded that using ilmenite minor-element chemistry as a tracer for sediment provenance is a valid technique, but they also cautioned that textural features of ilmenite in colluvium may be distinct from those in the parent rock. Secondary phases, such as anatase, goethite and hematite in soil profiles form, in part, from the alteration of ilmenite. The significance of ilmenite chemistry in diamond exploration is reviewed by Nowicki et al. (2007, this volume).

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