Assessing the sediment factory: The role of single grain analysis

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Abstract

Type and amount of sediment generation are intimately connected to tectonic and climatic processes active at the earth's surface today as well as throughout the geologic past. Detrital single grains (sand to very coarse silt sized) from well-dated sedimentary formations serve as mineral tracers in sedimentary systems and record the sediment-forming processes. In this review, a selection of individual methods available to extract petrogenetic and chronological information from detrital mineral grains is compiled. Emphasis is placed on techniques, concepts, and their possibilities and shortcomings in defining the type and geologic history of source rocks, as well as the rates and relative proportions at which sediments are being eroded and delivered to basins. Statistical issues intrinsically coupled to the interpretation of detrital single-grain distributions are highlighted, as well as new emerging techniques. These include geochronology of phases like e.g. titanite, monazite, or rutile to overcome the common restriction to apatite or zircon bearing lithologies, as well as any kind of double or triple dating to extract both high-T and low-T thermochronological information from the very same detrital grains. Mineral pairs are especially suited to quantify the relative contributions of well-defined source rocks or areas to the sediment when the two phases (i) occur in contrasting rock types, (ii) are relatively stable under sedimentary conditions, and (iii) allow for extracting significant and detailed information on source rock petrology and chronology. In general, however, multi-method approaches are the only way to overcome ambiguous information from the sedimentary record. In combination with either independent information on sediment flux or erosion rates derived from single-grain thermochronology, the sediment-forming processes as well as their controlling mechanisms and overall geologic settings can be properly assessed.

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1. Introduction

The sediment factory, i.e. the system that generates detrital material from solid rocks and delivers sediment to sedimentary basins, is controlled by a variety of processes including the lithology of the source rocks, tectonic activity, relief and climate in the source area, as well as the modes of sediment transport, dispersal, and alteration on transit (e.g. Johnson, 1993; Weltje and von Eynatten, 2004). The lithology of the source rocks defines the “potential” detritus spectrum, i.e. the types and relative abundances of minerals and composite grains that may enter a specific sedimentary system. Tectonics, relief, and climate control the amount and rates of sediment delivery to the drainage basin and sediment transport systems. Within the latter, sediment is abraded and chemically weathered depending on transport mechanisms and climate, as well as fractionated according to grain size, shape, and density. The complexity of the processes involved implies that largely similar sediment may be produced from different sources as well as different sediments may be produced from similar source rocks. Despite all these pitfalls, however, reconstructing sediment provenance in all its facets constitutes a widely used approach in geosciences, mainly because (i) distinct breaks and/or trends observed in the detrital record (that reflect distinct events and/or processes in the hinterland) can be precisely dated by stratigraphic means, and (ii) technical advances allow for extracting more and more sophisticated information from single detrital grains such as host rock lithology (e.g. Zack et al., 2004b; Morton et al., 2004), metamorphic conditions (e.g. Triebold et al., 2007), crystallization and cooling ages (e.g. Sircombe, 1999; Sha and Chappell, 1999; von Eynatten et al., 1999; Mikes et al., 2009), and cooling and exhumation rates of the host rocks (e.g. Whipp et al., 2009).

Basically sedimentary provenance analysis is a deductive approach, trying to unravel the processes that generated the sediment under investigation from the characteristics of the sediment itself. Traditional modal analysis relies on bulk sediment composition based on petrography (modal composition of framework grains, e.g. Blatt, 1967; Dickinson, 1970; Ingersoll et al., 1984) or geochemistry (major and trace element composition, e.g. Pettijohn, 1963; Potter, 1978). The growing data base for different tectonic settings allowed for developing tectonic discrimination schemes based on bulk sediment composition (e.g. Dickinson and Suczek, 1979; Bhatia, 1983; Dickinson, 1985; Bhatia and Crook, 1986; Roser and Korsch, 1986). These unifying and frequently-used concepts in provenance analysis became recently challenged (Armstrong-Altrin and Verma, 2005; Weltje, 2006; Garzanti et al., 2007; Pe-Piper et al., 2008; von Eynatten et al., 2012) and should be used with great care. Besides high degrees of wrong classifications when applied to Neogene to modern systems (i.e. samples are assigned to incorrect tectonic settings), statistical flaws in the construction of both discriminating fields and confidence intervals became evident (Weltje, 2002; von Eynatten et al., 2002).

Following a few early attempts and statements (e.g. Krynine, 1946; Blatt, 1967) the first detailed studies on heavy mineral chemistry and detrital zircon dating date back to the 1980s (Morton, 1985; Dodson et al., 1988). Since then a wide range of analytical techniques has become available to study geochemical and isotopic composition of individual sand-sized grains. The principal advantage of single-grain studies is based on the assumption that differential fractionation of grains from a single mineral phase is negligible, i.e. variability within that mineral phase is considered to be not affected by fractionation due to mechanical and chemical processes in the sedimentary system (see Section 3 for some critical points regarding this assumption). The potential of single-grain techniques with respect to mineral chemistry in provenance research was first summarized by Morton (1991) and further developed towards so-called varietal studies, i.e. investigating the characteristics and variability of single grains of a single mineral phase (e.g. garnet, tourmaline, zircon). Initially morphological and other light-microscopic features and their variability within single mineral phases were also investigated (high-resolution heavy mineral analysis; cf. Mange-Rajetzky, 1995). The fast development of geochemical and isotopic techniques, especially regarding electron microprobe (EMP) and laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) and the ever-improving high spatial resolution (i.e. small beam diameter), has made these techniques the most prominent in the last decade (e.g. Najman, 2006; Foster and Carter, 2007; Kofler and Sylvester, 2007; Frei and Gerdes, 2009).

This review paper concentrates on accessory minerals (mainly heavy minerals) as they provide more distinct information from single grains on sediment sources in many cases. Typical sandstone framework grains such as quartz, feldspar (except for isotopic analysis), and lithoclasts will not be considered here. For detailed lithoclast classification studies as well as quartz cathodoluminescence studies we refer to, for instance, Garzanti and Vezzoli (2003) and Bernet and Bassett (2005), respectively. Regarding sediment grain size, we will focus on sand to very coarse silt sized detrital grains because this grain size range is (i) readily available from most sedimentary basins (in contrast to coarser-grained sediment), and (ii) allows for applying a wide range of analytical techniques which is not the case for finer grain sizes. This implies, however, that we will not consider pebble, cobble, or boulder sized material although such coarse material may provide important additional information on pressure–temperature–(time) paths of metamorphic clasts (e.g. Cuthbert, 1991; Spalla et al., 2009), or on the relation of age components to specific lithologic clast types (Dunkl et al., 2009).

Emphasis is placed on techniques, concepts, and their possibilities and shortcomings in defining the type and geologic history of source rocks, as well as the rates and relative proportions at which sediment is being eroded and delivered to the basins. Specific case studies which are often fraught with unique geological circumstances are beyond the scope of this paper that is more intended as a state-of-the-art methodological overview designed for researchers applying single-grain techniques to their respective geological problem. We will first review and evaluate the wealth of possible information extractable from single grains to characterize the nature and chronology of specific rocks and rock associations in the source area. Problems and pitfalls associated with the individual methods will be highlighted. We will further tackle the problems of sediment modification associated with weathering, transport, and deposition, and its possible effects on the significance of detrital single-grain studies. Finally, the link between sophisticated source rock information obtained from single-grains and the bulk sediment transfer from source to sink will be addressed.

2. Source rock characterization

Beyond basic discrimination of different sources and/or the detection of analog with known sources, single-grain analysis attempts to constrain source rocks and their geologic context from the detrital grains itself, i.e. information from a specific type of grain is used to detect (i) lithology and petrologic conditions of the source rocks, (ii) their ages of crystallization and/or metamorphism, and (iii) the timing of late stage cooling and exhumation to the surface as determined by low-temperature thermochronometers.

In principal, the techniques applied cover nearly all methods developed to study crystalline rocks, too. However, detrital grains have mostly lost their paragenetic context. Therefore, petrologic information on geothermometry and/or geobarometry relying on coexisting mineral pairs or triplets (e.g. Powell and Holland, 2008) cannot be applied to detrital sand grains. Instead, such information must be derived from the occurrence and characteristics of single phases that either reflect well defined metamorphic conditions like, for instance, glauconite or aluminum-silicates such as kyanite or sillimanite (e.g. Yardley, 1989; Evans, 1990), or provide thermobarometric information based on single phase geochemistry and some reasonable assumptions. The latter include Zr-in-rutile geothermometry (Zack et al., 2004a; Tomkins et al., 2007), celadonite content in muscovite (i.e. phengite geobarometry; Massonne and Schreyer, 1987), and Al-in-hornblende
igneous geobarometry (Hammarstrom and Zen, 1986; Ridolfi et al., 2010). Similarly, chronological information obtained from detrital single grains cannot be smoothly related to, for instance, a paragenetic sequence reflecting pressure–temperature–time evolution of metamorphic rocks (e.g. Villa, 2010).

Single-grain geochronological methods can be classified in two groups according to the closure temperatures ($T_c$) of the given mineral–method pairs (e.g. zircon $U$–$Pb$ or apatite ($U$–$Th$)/$He$). This kind of grouping is useful for our purpose, because the so-called high-temperature (high-$T$) chronometers refer to the age of igneous activity (such as zircon $U$–$Pb$ chronometry with $T_c$ above 900 °C; e.g. Dahl, 1997) as well as re-crystallization and cooling of metamorphic bodies at mid crustal levels (e.g. white mica $Ar$/$Ar$ or monazite ($U$–$Th$)/$Pb$ chronometry). This age data serve as fingerprints of major geodynamic events in the source terranes of the sediment (see Section 2.2.1). On the other hand the so-called low-temperature (low-$T$) chronometers (like apatite fission track or ($U$–$Th$)/$He$ methods) reflect cooling histories in shallow crustal levels. The latter data are, especially in tectonically active regions, related to exhumation processes and are thus strongly connected to sediment generation (see Sections 2.2.2 and 4.1).

A compilation of single-grain geochemical and geochronological methods that we consider most useful in assessing sedimentary systems is given in Table 1. This synopsis does not aim at listing all possible minerals for single-grain provenance analysis. It includes, however, some analytical techniques which are not yet used for provenance issues but have considerable potential for providing crucial information on parent rocks. Obviously the combination of petrogenetic and chronological information, if possible, has high potential for precise fingerprinting of sources as well as relating lithologic information to exhumation and erosion processes and rates (e.g. Ruiz et al., 2004; Foster and Carter, 2007).

2.1. Lithology and petrology

In this part we attempt to give an overview on detrital minerals that are well suited and have been used in constraining lithology and petrologic conditions of source rocks. We will approach the topic from the respective major types of source rocks instead of aiming at a comprehensive overview of the potential sources of individual detrital minerals (e.g. Mange and Morton, 2007), i.e. the question is: what tools do we have to constrain a specific type or subtype of rock using detrital minerals. We will focus on accessory minerals, thus, typical sand(stone) framework grains such as quartz, feldspar, and the various kinds of lithiclasts will not be considered here (see above). Unless indicated otherwise the information on typical host-rock lithology and paragenesis is taken from Deer et al. (1992), Mange and Maurer (1991), and Bucher and Frey (1994).

2.1.1. Single grain record of igneous source rocks

Accessory minerals that typically occur in clastic sediments and are well-suited to record weathering and erosion of igneous rocks comprise zircon, apatite and other phosphate minerals, tourmaline, amphibole, pyroxene, and titanite as well as less common phases like topaz, garnet, etc. Moreover, opaque phases such as ilmenite and magnetite frequently occur in igneous rocks and may survive sedimentary processes. Appearance and composition of these minerals strongly depend on the type of igneous parent rock and many of them may derive from metamorphic rocks as well. Therefore, single-grain techniques based on mineral chemistry must primarily focus on a clear discrimination between magmatic and metamorphic host rocks, and, furthermore, strive to unravel principal types (e.g. volcanic vs. plutonic, alkaline vs. subalkaline/calc-alkaline) and degrees of fractionation of the igneous source rocks.

Zircon is a prominent constituent of intermediate to felsic igneous rocks. It is one of the most common heavy minerals of sand-sized sediments and sedimentary rocks due to extreme stability against both mechanical abrasion and chemical weathering. Moreover, zircon is very stable up to high-grade metamorphism and often survives (and thus records) several orogenic cycles. Several studies have attempted to find systematic relations between host rock and zircon trace and rare earth element (REE) concentrations (e.g. Hoskin and Ireland, 2000; Belousova et al., 2002a). Results reveal that REE patterns of crustal zircon do not show a systematic contrast between zircons from disparate crustal rock types. Hafnium concentration in zircon generally increases with magmatic differentiation; however, variability within a single pluton may be huge (Hoskin and Schaltegger, 2003). Zircon with mantle affinity, derived from e.g. kimberlites or carbonatites, have distinctly different REE patterns that are flatter and have overall lower REE abundances compared to crustal zircon. Moreover, zircons from kimberlite have very low $U$ and $Th$ content (Krasnobaev, 1980; Belousova et al., 2002a). Hydrothermal zircon is enriched in trace elements and REE relative to magmatic zircon from the same rock (Hoskin, 2005). Zircons that fully recrystallized under high-grade metamorphic conditions are relatively depleted of cations less compatible with the crystal structure leading to, for instance, low Th/U ratios (<0.1) that are also typical for metamorphic zircon crystallized from partial melts (Rubatto, 2002; Hoskin and Schaltegger, 2003). In contrast, igneous zircons generally have Th/U ratios ≥0.5 but may be as low as 0.2 for less common rock-types such as kimberlites (Hoskin and Schaltegger, 2003; see e.g. Butler et al., 2011 for a recent application to detrital zircon). $Th$ concentration in zircon may be indicative of crystallization temperature (Watson et al., 2006), however, Fu et al. (2008) have demonstrated that factors other than temperature and $TiO_2$ activity control $Ti$ content in zircon. This problem became especially valid when dealing with detrital zircon. Other parameters to describe zircon variability may include color and morphology (Pupin, 1980; Vavra, 1993; Dunkl et al., 2001) as well as oxygen, lithium or hafnium isotopic composition (e.g. Valley et al., 1994; Knudsen et al., 2001; Gerdes and Zeh, 2006; Flowerdew et al., 2007; Bouvier et al., 2011). Combination of geochemical and/or morphological zircon variational studies with $U$–$Pb$-dating and/or low-temperature thermochronological techniques as described below, is very promising and has been applied already in several case studies (e.g. Roback and Walker, 1995; Dunkl et al., 2001; Garver and Kamp, 2002; Bahlburg et al., 2009).

Tourmaline has, like zircon, an extremely durable character against both mechanical abrasion and chemical weathering and is, thus, prone to sediment recycling. Tourmaline is primarily derived from granitoid-type rocks and their differentiates, but also common in metamorphic, mostly metapelitic rocks. The former group is generally of scholr (Fe-rich endmember) to elbaic (Al, Li-rich endmember) composition and can be discriminated from metasedimentary tourmaline by means of molecular proportions of Mg, Fe, Ca, and Al (Henry and Guidotti, 1985; Henry and Dutrow, 1992). Very high Mg:Fe ratios may additionally hint to metalutrmalafs and/or metacarbonates as source rocks. This approach has been widely used in sedimentary provenance analysis to unravel the major source of detrital tourmaline (e.g. von Eynatten and Gaupp, 1999; Morton et al., 2005). Interestingly, most studies have reported a strong predominance of tourmaline from metasedimentary rocks, although tourmaline is very common in granitoids and their differentiates. This general observation, however, might be biased by (i) inherited grain size effects (see Section 3) and/or (ii) a possibly higher stability of Mg-rich tourmaline against extreme weathering as reported by few studies (van Loon and Mange, 2007; Andò et al., 2012).

In igneous rock, apatite abundance generally correlates positively with phosphorus and negatively with silica content. Most igneous rocks contain traces of apatite with fluorapatite being more common in granitoid rocks and chlorapatite more common in basic rocks (Piccoli and Candela, 2002). The secondary anion content (i.e. $Cl$/$F$/$OH$ ratios) of detrital apatite can be used as a diagnostic parameter for the identification of magmatic source rocks (Araki et al., 1995). It is also relevant for fission track analysis because CI content impacts closure temperature (Green et al., 1986; see Section 2.2.2). It is noteworthy that euhedral
Table 1
Compilation of major single-grain geochemical and geochronological methods. References serve as an early example in which the method is applied to sedimentary systems (except for those methods that have not yet been applied to detrital grains).

<table>
<thead>
<tr>
<th>Method</th>
<th>Comment</th>
<th>Use</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amphibole</strong>&lt;br&gt;Geochem.</td>
<td>Major elements</td>
<td>Fingerprints and identification of high-P metamorphites or alkaline igneous rocks</td>
<td>++</td>
</tr>
<tr>
<td>Trace elements</td>
<td>Fingerprint of source area</td>
<td>+</td>
<td>Lee et al., 2003</td>
</tr>
<tr>
<td>REE</td>
<td>Magmatic processes</td>
<td>+</td>
<td>Decou et al., 2011</td>
</tr>
<tr>
<td>High-T chron.</td>
<td>Ar/Ar</td>
<td>T\textsubscript{c}: ~500 °C; uncert. higher than at micas</td>
<td>+</td>
</tr>
<tr>
<td><strong>Apatite</strong>&lt;br&gt;Geochem.</td>
<td>Trace elements</td>
<td>Fingerprint of source lithology</td>
<td>+</td>
</tr>
<tr>
<td>REE</td>
<td>Fingerprint of host magma</td>
<td>+</td>
<td>Foster and Carter, 2007</td>
</tr>
<tr>
<td>Cl/F/OH</td>
<td>Magma type</td>
<td>+</td>
<td>Árkai et al., 1995</td>
</tr>
<tr>
<td>Nd isotopes</td>
<td>Proxy for magmatic suites</td>
<td>++</td>
<td>Bizzarro et al., 2003</td>
</tr>
<tr>
<td>Sr isotopes</td>
<td>Proxy for magmatic suites</td>
<td>o</td>
<td>Chew et al., 2011</td>
</tr>
<tr>
<td><strong>High-T chron.</strong>&lt;br&gt;U–Pb</td>
<td>T\textsubscript{c}: ~450–550 °C</td>
<td>o</td>
<td>Laslett et al., 1987</td>
</tr>
<tr>
<td><strong>Low-T chron.</strong>&lt;br&gt;(U–Th)/He (AHe)</td>
<td>T\textsubscript{c}: ~55–70 °C</td>
<td>+</td>
<td>Stock et al., 2006</td>
</tr>
<tr>
<td>Fission track (AFT)</td>
<td>T\textsubscript{c}: ~90–120 °C; single-grain ages uncertain in post-Miocene time</td>
<td>+++</td>
<td>Laslett et al., 1987</td>
</tr>
<tr>
<td><strong>Other</strong>&lt;br&gt;External morphology</td>
<td></td>
<td></td>
<td>Dunkl et al., 2005</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Crystallographic characterization</td>
<td>o</td>
<td>Zattin et al., 2007</td>
</tr>
<tr>
<td>CL spectroscopy</td>
<td>REE and internal structure</td>
<td>o</td>
<td>Kempe and Götzé, 2002</td>
</tr>
<tr>
<td><strong>Epidote</strong>&lt;br&gt;Geochem.</td>
<td>Nd, Sr isotopes</td>
<td>Fingerprint of source area</td>
<td>+</td>
</tr>
<tr>
<td>O isotopes</td>
<td>Magma/metam. discrimination</td>
<td>o</td>
<td>Keane and Morrison, 1997</td>
</tr>
<tr>
<td><strong>Fe–Ti-oxides</strong>&lt;br&gt;Geochem.</td>
<td>Major elements, internal structure</td>
<td>Fingerprint of source area; magma/metam. discrimination</td>
<td>+</td>
</tr>
<tr>
<td><strong>Garnet</strong>&lt;br&gt;Geochem.</td>
<td>Major elements</td>
<td>Metam. source discrimination</td>
<td>++</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Metam. source discrimination</td>
<td>+</td>
<td>Andò et al., 2009</td>
</tr>
<tr>
<td><strong>K-feldspar</strong>&lt;br&gt;Geochem.</td>
<td>Pb isotopes</td>
<td>Fingerprint of source area</td>
<td>++</td>
</tr>
<tr>
<td>Low-T chron.</td>
<td>Ar/Ar</td>
<td>T\textsubscript{c}: ~250–150 °C</td>
<td>+</td>
</tr>
<tr>
<td><strong>Monazite</strong>&lt;br&gt;Geochem.</td>
<td>REE, Sm/Nd</td>
<td>Fingerprint of source area</td>
<td>+++</td>
</tr>
<tr>
<td>High-T chron.</td>
<td>(Th–U)/Pb(total) by EMP</td>
<td>Mainly for pre-Mesozoic ages</td>
<td>+++</td>
</tr>
<tr>
<td>Th–U/Pb by SIMS or LA-ICP-MS</td>
<td>Applicable also to Mesozoic and Cenozoic ages</td>
<td>++</td>
<td>Hietpas et al., 2010</td>
</tr>
<tr>
<td><strong>Low-T chron.</strong>&lt;br&gt;(U–Th)/He (MHe)</td>
<td>Final cooling</td>
<td>o</td>
<td>Stockli et al., 2007</td>
</tr>
<tr>
<td><strong>Other</strong>&lt;br&gt;Internal structure</td>
<td>Magma/metam. discrimination</td>
<td>+</td>
<td>Boyce et al., 2006</td>
</tr>
<tr>
<td>Spinel</td>
<td>Geochem.</td>
<td>Major elements</td>
<td>Magma type and evolution</td>
</tr>
<tr>
<td><strong>Pyroxene</strong>&lt;br&gt;Geochem.</td>
<td>Zr, Nb, and Hf isotopes</td>
<td>Geothermometry, proxy for bulk rock geochemistry</td>
<td>++</td>
</tr>
<tr>
<td><strong>Rutile</strong>&lt;br&gt;Geochem.</td>
<td>Zr, Nb, and Hf isotopes</td>
<td>Geothermometry, proxy for bulk rock geochemistry</td>
<td>+</td>
</tr>
<tr>
<td><strong>Spinel</strong>&lt;br&gt;Geochem.</td>
<td>Major elements</td>
<td>Magma/metam. discrimination</td>
<td>++</td>
</tr>
<tr>
<td><strong>Titanite</strong>&lt;br&gt;Geochem.</td>
<td>Al/Fe\textsuperscript{3+}, REE, trace Th/U ratio</td>
<td>Magma/metam. discrimination</td>
<td>o</td>
</tr>
<tr>
<td>High-T chron.</td>
<td>U–Pb</td>
<td>High common Pb content, mainly for pre-Mesozoic ages</td>
<td>+</td>
</tr>
<tr>
<td>Low-T chron.</td>
<td>Fission track</td>
<td>T\textsubscript{c}: ~300 °C</td>
<td>o</td>
</tr>
<tr>
<td><strong>Tourmaline</strong>&lt;br&gt;Geochem.</td>
<td>Major elements</td>
<td>Magma (pegmatitic)/metamorphic discrimination</td>
<td>++</td>
</tr>
<tr>
<td>B and Li isotopes</td>
<td>Chemistry of co-genetic fluids</td>
<td>+</td>
<td>Shabaga et al., 2010</td>
</tr>
<tr>
<td>White mica&lt;br&gt;Geochem.</td>
<td>Phengite content</td>
<td>For detection of HP metamorphites</td>
<td>++</td>
</tr>
<tr>
<td>High-T chron.</td>
<td>Ar/Ar</td>
<td>T\textsubscript{c}: ~400 °C typically used for grains &gt;250 µm</td>
<td>++</td>
</tr>
<tr>
<td>Rb/Sr</td>
<td>Initial isotope ratio needs to be estimated</td>
<td>+</td>
<td>Chen et al., 2009</td>
</tr>
</tbody>
</table>
volcanic apatite grains derived from syn-sedimentary volcanic ashes play a prominent role in correlating sedimentary successions (Dunkl et al., 2005).

Apatite may concentrate a high proportion of the whole-rock REE as well as trace elements like Sr, U, Th, and Y. Parameters such as total REE concentration, LREE enrichment, LREE/HREE ratios, Eu anomaly and some trace element concentrations (mainly Sr, Y and Mn) reflect fractionation within a wide range from ultramafic to highly fractionated granitoid rocks and allow the differentiation between different types of igneous host rocks (Dill, 1994; Sha and Chappell, 1999; Belousova et al., 2002b; Jennings et al., 2011). Their database, however, is not sufficiently comprehensive to account for the huge variety of apatite-bearing source rocks, especially regarding metamorphic rocks (Spear and Pyle, 2002; Morton and Yaxley, 2007). That means provenance discrimination based on apatite geochemistry appears to be well suited to discriminate different sources or to prove similarity of sources (e.g., von Eynatten et al., 2008). However, the exact identification of the lithologic and geochemical character of a given source solely by apatite mineral chemistry is hindered until a comprehensive database is established.

Beyond element concentration, detrital apatite grains are well suited to preserve stable and radioactive isotope signals of their host rock. For instance, O and Nd values can be measured on single detrital grains and provides information on composition and age of the source terrains (e.g. Foster and Carter, 2007). Other techniques such as strontium isotope ratio as a petrographic discriminator and U–Th–He or ZHe as dating techniques are more restricted to igneous and metamorphic rocks whereas the highest Mn, Mg, and Al concentrations were restricted to igneous rocks (though overlap between isotope systems is not always complete). The higher TiO₂ content of ilmenite from metamorphic rocks is corroborated by further studies (e.g., Schneiderman, 1995; Bernstein et al., 2008). Concentrations of TiO₂ > 50 wt.% are indicative for iron loss through weathering and oxidation and development towards pseudotachylite (Bernstein et al., 2008).

Grigsby (1990) used the relative proportions of optically defined homogeneous grains from magnetite–ulvöspinel solid solution series (TiO₂ max. ~25 wt.%) vs. grains with magnetite–ilmenite intergrowths vs. grains with exsolution of ulvöspinel or pleonaste ([Mg, Fe]Al₂O₄) to discriminate between volcanic and plutonic rocks from felsic to mafic/ultramafic compositions. In the case of homogenous grains, single grain geochemical analysis allowed for clear-cut discrimination between felsic plutonic and volcanic, intermediate volcanic, and mafic plutonic rocks based on Ti and V concentrations and Mg/Al ratios. For texturally homogenous ilmenite grains, i.e. ilmenite–hematite solid solution series with TiO₂ > 30 wt.%, Grigsby (1992) observed a well defined discrimination between mafic and felsic igneous sources (86% correct classification). This classification is based on six chemical elements, the main discriminants being Mn (high in felsic rocks) while Ti and Cr are relatively high in basic rocks. Other studies reveal high concentrations of elements like Mg, Cr, or V in ilmenite as indicators for basic to ultrabasic sources (Schneiderman, 1995; Darby and Tsang, 1987). However, single chemical spot analyses of Fe–Ti oxides have to be treated with care as complex intergrowth patterns are frequent and may produce considerable scatter in the data (e.g. Decou et al., 2011). Moreover, Fe–Ti oxides are prone to alteration and the types and paragenesis of alteration products strongly depend on the geochemical environments during diagenesis (Morad and Aldahan, 1986; Weibels and Friis, 2004, 2007), limiting their application to provenance studies of ancient sediments and sedimentary rocks unless these effects are observed and can be accounted for.

The huge variety in types and composition of chain silicates provides a versatile tool in discriminating source rocks based on major (Ruffini et al., 1997; Krawinkel et al., 1999; Barbieri et al., 2003), trace (e.g. Lee et al., 2003) and rare earth elements (e.g. Decou et al., 2011). Pyroxene is most common in igneous rocks ranging from ultrabasic to intermediate in composition, however, some common varieties such as hypersthene and augite are typical constituents in high grade mafic gneisses and granulites. If a volcanic origin of the detrital grains could be demonstrated, type of host magma and tectonic setting could be inferred based on clinopyroxene major and trace element composition (Nisbet and Pearce, 1977; Leterrier et al., 1982; Krawinkel et al., 1999). Amphibole classification based on major element concentration (Leake et al., 1997) or color (Garzanti et al., 2004) is helpful in terms of discrimination of different sources, but often remains ambiguous with respect

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### Table 1 (continued)

<table>
<thead>
<tr>
<th>Method</th>
<th>Comment</th>
<th>Use</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zircon</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geochem.</td>
<td>REE, trace elem.</td>
<td>Fingerprint of source lithologies</td>
<td>+</td>
</tr>
<tr>
<td>HF isotopes</td>
<td>Modell ages, igneous affinity</td>
<td>+</td>
<td>Knudsen et al., 2001</td>
</tr>
<tr>
<td>O isotopes</td>
<td>Chemistry of co-genetic fluids</td>
<td>+</td>
<td>Valley et al., 1994</td>
</tr>
<tr>
<td>Li isotopes</td>
<td></td>
<td>+</td>
<td>Ushikubo et al., 2008</td>
</tr>
<tr>
<td>U/Th</td>
<td>Magm./metam. discrimination</td>
<td>+</td>
<td>Rubatto, 2002</td>
</tr>
<tr>
<td>High-T chron.</td>
<td>U–Pb</td>
<td>Tₐ : magmatic crystallization</td>
<td>+ + +</td>
</tr>
<tr>
<td>Low-T chron.</td>
<td>Fission track (ZFT)</td>
<td>Tₐ : ~240–280 °C; method is biased in pre-Mesozoic ages</td>
<td>+ + +</td>
</tr>
<tr>
<td>Other</td>
<td>(U–Th)/He (ZHe)</td>
<td>Tₐ : ~150–180°C</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Shape, crystal typology, color</td>
<td>Discrimination of different magmatic sources and mature (meta)sediments</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dunkl et al., 2001</td>
</tr>
</tbody>
</table>

Abbreviations: AFT: apatite fission track, AHe: apatite (U–Th)/He, CL: cathodoluminescence, EMP: electron microprobe, REE: rare earth element distribution, RhE: rutile (U–Th)/He, ZHe: zircon (U–Th)/He.

+ + +: rough estimate of the frequency the method is used in single-grain provenance studies.

*: the technique is potentially useful for provenance studies, but not yet applied as a single-grain method. (it is in the experimental stage and/or used only on basement rocks, typically on multi-grain aliquots.)
to source rock identification (e.g. Durn et al., 2007). For instance, minerals from the hornblende series (sensu latu) encompassing such diverse types as edenite, tschermakite, pargasite, hastingsite, etc. occur in a wide variety of basic to acidic magmatic rocks, but also in many metamorphic rocks like schists, gneisses and especially in amphibolites. Some other amphiboles are more indicative for source rocks, for instance, blue sodic amphibole riebeckite is commonly found in alkaline intrusive rocks and titanium-rich kaersutite typically occurs in alkaline volcanic rocks. For a more detailed review of chain silicates in provenance studies we refer to Mange and Morton (2007), for some metamorphic amphiboles see also Section 2.1.2.

In principle, it is possible to trace the evolution of a volcanic system via detrital minerals in the sedimentary record given that detailed knowledge on partition coefficients between minerals and melt is available (e.g. Green, 1994; Albarede, 1996), i.e. knowing mineral composition (e.g. pyroxene, amphibole) and mineral-melt partition coefficients allows for calculating a coexisting theoretical melt composition (Ridolfi and Renzulli, 2011). This has been used, for instance, in a case study of Paleozoic basalts and gabbroic sills in Morocco to demonstrate (i) a similar parental magma for clinopyroxene from both rock types, and (ii) a subduction related tectonic settings of these magmas (Driouch et al., 2010). Trends in the composition of detrital grains in a sedimentary succession in time and space might thus be interpreted in terms of, for instance, differentiation and migration of a volcanic system through time and space. Some aspects may perturb this straightforward approach such as (i) calculated melt composition may differ from the mineral’s host rock composition, (ii) crystallization history might be too complex to be expressed by a single partition coefficient (e.g. Marks et al., 2004), and/or (iii) partition coefficients are a function of major element composition of the melt which is unknown or poorly constrained. In sedimentary provenance analysis these techniques have yet been rarely applied. In a case study from the Tertiary Andean forearc basin in southern Peru, Decou et al. (2011) observed an upsection increase of Sm/Yb and Dy/Yb ratios in detrital amphibole. This change reflects a larger scale phenomenon of the Central Andean orocline related to crustal thickening and corresponding magma evolution under increasing pressure (Mamani et al., 2010). The use of chain silicates as single-grain indicator for particular source rocks is generally hindered because (i) the attribution of individual grains to metamorphic or igneous host rocks remains often ambiguous (see above), and (ii) chain silicates show high degree of instability in sedimentary systems, both mechanico-chemical and chemical, with pyroxenes being in general even less stable than amphiboles (Mange and Maurer, 1991). This is especially unfortunate for the detection of basic volcanic rocks that lack many of the other more stable minerals mentioned before.

Titanite occurs in many igneous rocks, and frequently constitutes the main Ti-bearing phase in intermediate to felsic plutonic rocks typically having high oxygen fugacity, where it forms sometimes well developed, several mm-sized crystals. The trace element signature can be potentially used for the estimation of the composition of the host magma (Tiepolo et al., 2002). Titanite, however, is also present in metamorphic rocks where it mainly indicates basic lithologies rich in ferromagnesian minerals. Fe/Al and U/Th ratios of titanite are well suited to discriminate these two major genetic types (Aleinikoff et al., 2002), however, this has not yet been applied to detrital titanite.

Almandine garnet composition from calc-alkaline volcanic rocks (mainly andesites, dacites, rhyolites) has been used to discriminate between magma types and crystallization depth (Harangi et al., 2001). This study also showed that considerable overlap exists between garnet derived from S-type magmas and garnet from metapelites (see also Mange and Morton, 2007). Garnet from deep-seated mantle-derived rocks could be detected on the basis of Ca and Cr content (Schulze, 2003; Grütter et al. 2004). Such garnets, however, are pretty rare and the overwhelming majority of garnets are univocal of metamorphic origin (see Section 2.1.2).

Ultradextrous rocks are mainly composed of olivine and pyroxene, however, these minerals are among the most unstable in the sedimentary cycle. The erosion of ultradextrous rocks is thus best recorded by serpentine or serpentine lithoclasts reflecting the common alteration product of olivine and pyroxene, and by chrome spinel being a main accessory component in peridotites. The chemistry of detrital chrome spinel has been intensively used to further constrain the type and tectonic setting of the host rocks (for a review of case studies and the main discrimination schemes we refer to Mange and Morton, 2007). Although the major trends have been documented, it must be noted that most of the studies on detrital chrome spinel chemistry reveal large scatter in the data (e.g. Pober and Faupl, 1988; Argylean, 1996; Coolenbou et al., 1997; Ganssloser, 1999; Lenaz et al., 2000, 2003; Faupl et al., 2006b; Lužar-Oberit et al., 2009), making a clear-cut differentiation of the sources and their genetic evolution sometimes ambiguous. This is most likely due to the fact that many of these studies are related to the erosion of suture zones in collisional settings where ultradextrous slices having different petrogenesis were obducted and/or exhumed and are frequently mixed together in melange-type units during subsequent convergence and deformation. Attention must be paid to the fact that chrome spinel belongs to the very stable heavy minerals and is prone to be recycled from older sedimentary rocks (e.g. von Eynatten, 2003). This may even increase scatter in detrital chrome spinel data.

### 2.1.2. Single grain record of metamorphic source rocks

The discrimination of metamorphic vs. igneous origin has been already addressed in the previous section. The most prominent methods include tourmaline major element composition and zircon Th/U ratios, and with several limitations, ilmenite, phosphates, garnet, titanite, and chain silicate composition (see Section 2.1.1).

Mineral species and assemblages indicative for metamorphic rock type or grade depend on the protolith composition, temperature (T), pressure (P), and fluid characteristics (X). All these parameters are primarily unknown when working with detrital minerals. Index minerals such as staurolite, kyanite, sillimanite and chloritoid are valid only for certain settings, i.e. Barrovian-type metamorphism of Al-rich pelitic rocks. For similar protoliths, cordierite and andalusite indicate low pressure–high temperature metamorphic conditions (but note that cordierite may also occur in peraluminous granites). Further index minerals typically include glaucophane, lawsonite, omphacite and actinolite. The former three are diagnostic for high-pressure metamorphic rocks, with glaucophane being especially used to prove the erosion of blueschist facies rocks (e.g. Mange-Rajetzky and Oberhansli, 1982; von Eynatten et al., 1996; Faupl et al., 2002). Members of the tremolite–actinolite series are common in metabasic rocks and in carbonate-bearing metamorphic rocks, as well as in metamorphosed igneous rocks covering a wide range from hydrothermal (epithemal) conditions through prehnite–pumpellylite facies up to amphibolite facies. Most metamorphic rocks, however, are characterized by diagnostic mineral assemblages rather than by a certain index mineral, and these assemblages are prone to be obscured during weathering, transport, and sediment mixing (see Section 3). Apart from the mere occurrence of specific minerals, single grain characteristics are used to deduce the metamorphic origin of detrital grains and to further unravel the type of metamorphic host rock. Variations in amphibole color and Ti-content have been successfully used to trace variations of metamorphic grade in amphibolite to granulite facies rocks of the Alps (Garzanti et al., 2004, 2006b; Andò et al., in review).

For the characterization of different metamorphic source rock types several single-grain geochemical techniques are available. Rutile is a frequent accessory mineral in medium to high-grade metamorphic rocks and its trace element systematics allow for highly significant separation between metapelitic and metamafic host rocks. Several slightly contrasting discrimination schemes have been proposed (Zack et al., 2004b; Triebold et al., 2007; Meinhold et al., 2008). The most recent one is built on an increased data base and a multivariate statistical
test of discrimination success, and attains 94 to 95% of correctly classified rutile grains (Triebold et al., in press). Although this is an excellent result in terms of statistics, misinterpretations are still possible if (i) the number of analyzed grains is too small, (ii) extraordinary rocks are involved such as ultra-high-pressure eclogite from within-plate basaltic protolith (i.e. the low degree of melting causes high Nb/Ti ratio of the basalt that in turn results in high Nb rutiles; Triebold et al., 2007), and/or (iii) polymorph of TiO₂ minerals is not considered properly (Triebold et al., 2011).

Epidote group minerals are typical for low to medium grade metamorphic rocks (mainly greenschist to blueschist facies) where it replaces Ca-bearing silicates, especially plagioclase. In a case study of the Oligocene to Miocene North-Alpine Foreland Basin in Switzerland, Spiegel et al. (2002) could demonstrate that detrital epidote could be assigned to its crust-derived (metagranitoids) or mantle-derived (metabasalts) source rocks via trace element and Nd isotope signatures. Although almost entirely of metamorphic origin magmatic crystallization may form epidote in some granodiorite suites. Keane and Morrison (1997) demonstrated that the oxygen isotope composition of the epidote may be used as diagnostic tool to distinguish magmatic from subsolidus epidote. The method can also be applied to single grains.

Many metamorphic rocks contain abundant garnet group minerals covering a huge (P, T, X)-range from micaschists via amphibolites to eclogites. Compositional variation of garnet is also huge making it a prime candidate for source rock discrimination based on single-grain geochemistry. Reconstruction of the respective metamorphic host-rock type, however, is problematic because similar parageneses may contain different garnets and vice versa depending on protolith composition and metamorphic conditions. Thus considerable overlap in garnet composition from different rock types is obvious (see review in Mangen and Morton, 2007). Several case studies, however, showed that garnet composition may in fact fingerprint specific source lithologies at regional scale (e.g., Morton et al., 2004). These empirical observations call for a robust garnet discrimination scheme built on a comprehensive data base and multivariate statistics.

The methods mentioned before are valuable for constraining source rock and/or protolith type but only roughly narrow down metamorphic grade, i.e. pressure and temperature conditions. Thermobarometry of metamorphic rocks usually requires coexisting mineral pairs such as garnet–biotite or garnet–clinopyroxene that inherently do not exist in sediment (except for some extremely rare cases of, e.g. biotite inclusion in detrital garnet). Single-grain geothermobarometers are rare and usually fraught with additional assumptions on paragenesis. A straightforward approach provides Zr-in-rutile thermo(baro)metry that is based on Zr content in rutile assuming equilibrium with quartz and zircon during rutile growth (Zack et al., 2004a). This assumption is pretty reasonable for metamorphic rocks, and it could be demonstrated that the technique also works for mafic rocks (Zack and Luvizotto, 2006; Triebold et al., 2007). Experimental studies have further refined Zr-in-rutile thermometry and included a pressure component (Watson et al., 2006; Tomkins et al., 2007). Some advice for treating the pressure issue and calculated temperature distributions is given in Triebold et al. (in press). Related techniques such as Ti-in-zircon thermometry (Watson et al., 2006) have not yet been applied to studies in sedimentary systems, because factors other than (peak) temperature and TiO₂ activity may control Ti content in zircon (Fu et al., 2008; Liu et al., 2010).

Another single grain geo(thermo)barometric method that has been applied in sedimentary studies is phengite geobarometry (i.e. Mg-celadonite content in white mica), that is thought to be largely pressure-controlled in parageneses including phengite, K-feldspar, phlogopite and/or chlorite, and quartz (Massonne and Schreyer, 1987). Including other paragenetic phases may complicate the scenario but for most parageneses phengite geobarometry still yields minimum pressures (e.g. Oberhansli et al., 1995; Zhu and Wei, 2007), implying that a significant increase of Si and Mg content in white mica is usually indicative of increasing pressure in the source rocks. Detrital phengite geobarometry has been used, for instance, to constrain the erosion of high-pressure metamorphic rocks (e.g. von Eynatten et al., 1996; Willner et al., 2004; Chen et al., 2009), and to prove progressive exhumation of deeper seated rocks as documented in foreland basin sequences (e.g. von Eynatten and Wijbrans, 2003; Carrapa et al., 2004).

2.1.3. Single grain record of recycled sedimentary rocks

One of the major motivations to apply single-grain techniques is that they are thought to behave inert with respect to processes in the sedimentary and diagenetic environment. Thus, single grains themselves usually cannot prove their origin from recycled sedimentary rocks unless (i) grain type and texture clearly point to syn-sedimentary or diagenetic origin (e.g. sedimentary lithoclasts, glauconite, anatase), (ii) grains show authigenic rims (e.g. reworked quartz overgrowths, tourmaline, apatite), and/or (iii) their composition can be precisely linked to similarly composed grains from older sedimentary rocks (e.g. von Eynatten, 2003; von Eynatten et al., 2008). Evidence for sediment recycling is generally derived from bulk sediment composition or heavy mineral data such as overall petrographic maturity, zircon–tourmaline–rutile index, or specific bulk sediment trace element patterns indicative of, for instance, zircon or chrome spinel enrichment due to their high stability within the sedimentary cycle.

2.2. Single-grain geochronology

This part concentrates on the chronologic information extractable from single detrital grains, starting with the relevant high-T thermochronometers, followed by low-T thermochronometers, newly emerging techniques including double and triple dating, and finally, several issues regarding the statistics of single-grain age distributions will be addressed.

2.2.1. Ages of crystallization and cooling ages in metamorphic conditions

Single-grain geochronology provides highly diagnostic information on the source areas of siliciclastic sediments (e.g. Fedo et al., 2003). The age data may be even more specific than the information carried by the composition of heavy mineral assemblages only, or by varietal studies of certain mineral species. Combinations of both geochronology and heavy mineral analysis are most promising (e.g. von Eynatten et al., 1996; Mikes et al., 2008). The result of a detrital geochronologic survey is an age distribution, where the number of dated grains as well as the method of grain selection is strongly linked to the significance of the results (e.g. Vermeesch, 2004; Andersen, 2005). The individual age components (well defined clusters of single-grain ages) usually allow for exact identification of given basement units as sediment sources. Typically acid to intermediate (meta)igneous rocks as well as quartz-rich and/or mica-bearing (meta)sedimentary formations can be traced by datable detrital minerals from the sedimentary record.

2.2.1.1. Zircon U-Pb geochronology

Zircon concentrates uranium during crystallization from a melt while lead is largely incompatible with the crystal structure of zircon and, thus, the initial non-radiogenic Pb content is typically very low. This and the high closure temperature (ca. 750 °C; Spear and Parrish, 1996) make zircon the most prominent mineral for U-Pb geochronology. Zircon U-Pb geochronology was one of the first dating techniques applied to detrital minerals. This dates back to the 1980s (e.g. Dodson et al., 1988; Gehrels et al., 1995), and also focuses on dating the oldest zircons on Earth (Froude et al., 1983; Wilde et al., 2001). Uranium content of zircon is typically in the range of several hundred ppm and allows for precise single-grain dating by thermal ionization mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS) and laser ablation (LA) ICP-MS techniques (Kössler and Sylvester, 2007; Gehrels et al., 2008; Frei and Gerdes, 2009). In the last decade the majority of the detrital zircon U-Pb ages were generated by LA-ICP-MS because of considerable progress regarding sensitivity
monazite geochronology can register more thermo-tectonic events in the source areas. This advantage may lead to a better resolution in provenance studies, because zircon U–Pb dating is prone to not fully record multiple thermal events (Hietpas et al., 2010).

Apatite is less suitable for U–Pb single-grain geochronology than monazite, because the actinide contents are several magnitudes less, and the apatite always concentrates lead. The high proportion of common lead allows U–Pb geochronology typically for multi-grain analyses in basement samples (Chew et al., 2011), but the method obviously bears potential for dating single detrital crystals.

2.2.1.3. U–Pb geochronology of titanium minerals. The most relevant minerals are titanite and especially rutile. Titanite occurs in intrusive rocks as well as some volcanics of intermediate to acid composition (dacite, trachyte, rhyolite), while chlorite–mica–garnet rich schists and gneisses are the most important titanite-bearing metamorphic rocks. Moreover, metabasalts frequently contain well developed titanite crystals. Metabasic rocks and their detection from the sedimentary record are crucial in orogenic reconstructions, but its constituents are comparatively unstable and are not datable by most geochronological methods including the commonly used zircon U–Pb chronometer. The occurrence of titanite in such typically zircon-free lithologies allows for dating metamorphism of metamorphic rocks. Titanite, however, has variable but sometimes high common lead content (Frost et al., 2000). Therefore single-grain U–Pb dating can hitherto be performed with acceptable uncertainty for pre-Mesozoic ages only (McAteer et al., 2010).

Rutile belongs like zircon to the ultrastable heavy minerals and is thus common in siliciclastic sediments. Rutile is mainly derived from metamorphic rocks, especially upper amphibolite to granulite facies Ca-poor rocks and eclogites (Force, 1991), but granites, pegmatites and hydrothermal quartz veins may also contain rutile crystals (see review in Meinhold, 2010). Uranium content may be several tens of ppm depending on the geochemical character of the host rock, but may be rather low in metamorphic rocks (e.g. eclogites). Closure temperature for Pb diffusion in rutile is a currently debated issue but broadly ranges from 400 to 600 °C depending on cooling rate (Vry and Baker, 2006; Kooijman et al., 2010; Blackburn et al., 2011; Zack et al., 2011). U–Pb geochronology can be principally performed on detrital single grains by in-situ analytical techniques, because thorium and common lead contents are usually low (Mezger et al., 1989). Along with recent methodological developments of in situ LA-ICP-MS rutile dating regarding common lead correction and improved mineral standards (Zack et al., 2011), detrital rutile U–Pb geochronology has become a powerful additional tool in assessing source area geology (Meinhold et al., 2011; Okay et al., 2011). Rutile analysis has the additional advantage of being able to combine U–Pb geochronology with further single-grain information regarding host rock lithology and thermometry (see Section 2.1.2) as well as low-T thermochronometry (e.g. (U–Th)/He; see Section 2.2.3).

2.2.1.4. Ar/Ar geochronology of white mica. White mica is the most common K-bearing mineral phase in metamorphic rocks. Mineral growth starts already under deep-burial diagenetic conditions and the stability field of muscovite–phengite covers nearly all metamorphic facies until the breakdown isothersms. White mica is chemically rather stable (especially when compared to biotite), but resistivity to mechanical forces is poor due to excellent cleavage and low hardness. Its tabular shape, however, causes contrasting hydrodynamic behavior and transport mechanisms compared to most other detrital grains and only rare collisions with, for instance, durable quartz grains. White mica is most commonly found in water-lain arenites and coarse siltstones, and is usually lacking in eolian deposits.

The high potassium content of white mica generates precisely measurable amounts of argon within a relatively short time even in small crystal flakes. The closure temperature of this method is in the temperature range of upper greenschist to lower amphibolite facies. Thus single-grain Ar/Ar geochronology has become a popular method

**Fig. 1.** Approximate throughput and costs of the major single grain geochronological methods estimated in 2012. The cost ranges are indicative, calculated mainly for academic co-operations (the compilation is based on personal communications and on diverse web pages of universities and research laboratories).
in detrital geochronology regarding both source rock fingerprinting as well as derivation of apparent cooling rates (e.g. Copeland et al., 1990; von Eynatten et al., 1996; 1999; Najman et al., 1997, Stuart, 2002; von Eynatten and Wijbrans, 2003; Hodges et al., 2005; Najman, 2006; Brewer et al., 2006). The most useful additional single-grain analytical tool is the determination of the phengite content of the dated mica flakes that allows for deriving, under certain assumptions, geobarometric information on the source rocks (Massonne and Schreyer, 1987). Because high-pressure metamorphic rocks are highly diagnostic for the evolution of a given drainage system, the combination of white mica Ar/Ar geochronology and phengite geobarometry is especially useful in provenance studies (von Eynatten et al., 1996; Sherlock et al., 2000; von Eynatten and Wijbrans, 2003).

Besides hydrodynamic fractionation care should be addressed to different grain size distributions of micas inherited from the source rocks because some mica-bearing schists (e.g. phyllites or fine-grained micaschists) do not yield proper crystals for Ar/Ar geochronology (Hodges et al., 2005; Ruhl and Hodges, 2005). Such scenario may lead to a complete lack of relevant age components and/or overestimation of contributions from specific rock types such as (meta)granitoid rocks providing coarse-grained and well-crystallized detrital mica. It must be also noted that recent progress in geochronology and petrology of white mica-bearing rocks has shown profound influence of retrograde metamorphic reactions occurring during decomposition on the resulting Ar/Ar-ages (Alaee et al., 2011). The frequently made assumption that white mica grains having survived the sedimentary mill (i.e. weathering, erosion, transport, diagenesis) are generally well-crystallized and homogenous, and thus well-suited for Ar/Ar-geochronology may not be always valid.

2.2.2. Low-temperature cooling ages

The previously elaborated high-T geochronometers allow for linking sedimentary strata to their source areas, and thus inferring geodynamic and paleogeographic reconstructions. The low-T thermochronological methods may add considerably to the source identification, however, their main contribution to assessing the sediment factory lies in immediate information on the exhumation processes at upper crustal levels (Cerveny et al., 1988). In order to reduce this biasing effect, detrital ZFT dating should be usually based on two, sometimes even four, differently etched crystal mounts (Hill et al., 2009). Moreover, high density of fission tracks in the lattice of old and/or high-U zircon crystals results in advanced degree of metamictization in the respective crystals. Therefore dating of pre-Mesozoic grains is difficult and age distributions are biased because old ages are generally under-represented (Naeser et al., 1987; Bernet and Garver, 2005).

2.2.2.1. Fission track dating of detrital zircon grains (ZFT). The effective closure temperature $(T_c)$ of the zircon fission track thermochronometer depends on the duration of the thermal event and on the degree of metamictization of the zircon crystals. In young, low-U zircons $T_c$ is around $280 \pm 50 \, ^\circ C$ (e.g. Yamada et al., 1995), however, some literature data indicate $T_c$ values as low as $200 \, ^\circ C$ in zircons having high density of alpha-recoil tracks (see compilation by Rahn et al., 2004). ZFT is widely used in sedimentary studies and frequently delivers crucial information on sediment provenance and geodynamics of the source region(s) (Hurford et al., 1984; Carter, 1999; Ruiz et al., 2004). The chemical durability of zircon allows ZFT dating even in extremely weathered and chemically transformed formations like bentonites or laterites where most other geochemical and mineralogical parameters are no more applicable (Winkler et al., 1990; Dunkel, 1992).

Quantitative interpretation of detrital ZFT ages, including estimation of sediment mass balance, must consider some crucial points in applying this geochronological technique. The proper chemical enlargement of the spontaneous fission tracks needs typically longer etching time in case of old zircon grains than in case of young grains. Thus, the preparation of the samples has a significant bias on the age distribution (Cerveny et al., 1988). In order to reduce this biasing effect, detrital ZFT dating should be usually based on two, sometimes even four, differently etched crystal mounts (Skei et al., 2009). Moreover, high density of fission tracks in the lattice of old and/or high-U zircon crystals results in advanced degree of metamictization in the respective crystals. Therefore dating of pre-Mesozoic zircons is difficult and age distributions are biased because old ages are generally under-represented (Naeser et al., 1987; Bernet and Garver, 2005).

2.2.2.2. (U-Th)/He dating of detrital zircon grains (ZHe). The closure temperature for zircon (U-Th)/He method (ca. 150 to 180 °C; Reiners, 2005) is significantly lower than that for ZFT thermochronometer, and approximately the high end of the diagenetic regime, i.e. detrital ZHe ages from sedimentary basins are usually not resetted. Therefore, and due to its high mechanical and chemical resistivity, ZHe dating is ideally suited to link near-surface exhumation processes to sedimentation events (Reiners et al., 2005; Miller et al., 2010; Cecil et al., 2010).

In the case of (U-Th)/He thermochronometry (same with apatite, see below) a fraction of the helium (i.e. the product of the radioactive decay) leaves the crystal by the so-called alpha ejection phenomenon (Farley et al., 1996). Thus the rims of the grains are always depleted in helium. This deficit in the daughter product can be modeled and corrected according to the size and shape of the dated grain (Hourigan et al., 2005). This straightforward approach is, however, biased in detrital ZHe dating when mineral grains are (partly) rounded. It is difficult to judge whether the rounding took place before the thermal overprint of the grain’s host rock (in an older sedimentary cycle) or if it is the sole result of the last source to sink transport. If this not resolvable by other (provenance) information, the degree of uncertainty in the ejection correction may be as high as several tens of percent (Farley et al., 1996). Another consequence of the alpha ejection is a lower size limit for datable zircon grains. If the width perpendicular to the crystallographic c-axis is less than ~70 μm the necessary correction is too high and, thus, the dating cannot deliver reliable ages.

2.2.2.3. Ar/Ar geochronology of K-feldspar grains. Potassium feldspar frequently forms a significant constituent of arenites, and similarly to white mica the high potassium content allows for single-grain Ar/Ar geochronology (Chetel et al., 2005; Vermeesch et al., 2009). The closure temperature is variable and depends on the ordered state of the lattice, but it is close to the closure temperature range of the zircon fission track thermochronometer (Shibata et al., 1990; Lovera et al., 1999). Both methods may thus complete each other particularly in cases were (i) the post-depositional thermal overprint is in the $T_c$-range of the these two geothermometers, or (ii) Paleozoic and older ages are expected, where the ZFT thermochronometer is biased.

2.2.2.4. Fission track dating of detrital apatite grains (AFT). Apatite is a common accessory mineral that occurs in many types of magmatic and metamorphic rocks (see above). AFT thermochronometry is a very popular method in geodynamic and geomorphologic studies of...
Herberer et al., 2011; see discussion in Gallagher et al., 1998). Moreover, the costs are relatively low along with high sample throughput (Fig. 1). The method is also frequently used in provenance studies because arenaceous sediments often contain apatite. Besides fingerprinting, the cooling ages derived from detrital apatite grains can be related to exhumation processes in the hinterland that in turn generated enhanced erosion and thus control sediment production (e.g. Dunkl et al., 2005; van der Beek et al., 2006; Herberer et al., 2011; see Section 4.1). The most relevant limitations of the method are threefold. First, single-grain AFT ages are less precise than ZFT ages. This is because zircon concentrates more uranium than apatite and consequently more fission tracks are produced through time. Thus apatite single-grain ages usually have higher uncertainty compared to zircon (Garver et al., 1999). This disadvantage is especially crucial for young AFT ages (post-Miocene) and/or low-uraniumapatites that can be dated with high uncertainty only. Secondly, apatite is soluble in acid pore water causing many coal or ore bearing formations to be bare of apatite. Thirdly, due to its low closure temperature AFT data are sensitive to post-depositional thermal overprint, which can rejuvenate the AFT ages and obscure the initial provenance signal. Such overprint may start already well below Tc, as the partial annealing zone spans from approx. 70 to 120 °C (e.g. Glaudow et al., 1986).

2.2.2.5. (U-Th)/He dating of detrital apatite grains (AHe). Theapatite (U-Th)/He thermochronometer (AHe) has the lowest currently known closure temperature (ca. 60 to 80 °C; Farley, 2000), and is thus very attractive in many fields of applications, especially regarding geomorphological studies (e.g. Wolf et al., 1997). The increase of helium even in low-U apatite is a rather rapid process making single-grain dating of relatively young ages technically feasible. The applicability of the AHe method is, however, strongly limited by the high requirements for datable grains that should (i) be completely intact, (ii) inclusion free, and (iii) yield a minimum size so that alpha ejection correction procedure can be applied with acceptable bias (e.g. Fitzgerald et al., 2006). Because of these limitations only a very minor part of the separated detrital apatite crystals can be dated implying that random sampling of a detrital, typically mixed grain population is hardly feasible. Moreover, the method has considerably lower sample throughput than AFT thermochronology (Fig. 1). Despite above listed pitfalls the detrital AHe method is increasingly used and has demonstrated its huge potential for quantification of erosion processes and sediment yield (Stock et al., 2006; Tranel et al., 2011).

2.2.3. Emerging techniques and multiple dating approaches

The rapid development of the in-situ analytical techniques (especially in the field of laser-ablation ICP-MS) allows for predicting ongoing increase of sensitivity and further reduction of detection limits, and thus the development and application of new techniques in single-grain geochronology. Therefore, we mention here also some geochronological methods that are typically used on basement rocks and/or on multi-grain aliquots, but will potentially become applicable also in provenance studies. These techniques include, for instance, Rb/Sr dating of individual mica flakes. Chen et al. (2009) already used this technique for provenance analysis of Carboniferous sedimentary rocks of the Qinling–Dabie orogenic belt. The most significant limitation of this method is that the initial isotope ratio needs to be estimated. At similar stage of development are techniques like oxygen isotopes of epidote to discriminate magmatic vs. metamorphic sources, or Sr isotopes of apatite as proxy for magmatic processes (see Table 1).

Although titanite is not a frequently reported and widespread heavy mineral, its dating can be very informative. Fission track and (U-Th)/He thermochronology of titanite dates cooling below closure temperatures of approximately 240–300 °C and 160–220 °C, respectively, and has been successfully used in basement studies (Coyle and Wagner, 1998; Reiners and Farley, 1999). (U-Th)/He thermochronology is also applicable to rutile having a closure temperature close to that of zircon (Stockli et al., 2007; Dunkl and von Eynatten, 2009). The particular importance of these Ti-mineral-based methods originates from their potential to date sediments that lack the typical phases used in low-T thermochronology (i.e. zircon, apatite). Further developments include laser microprobe (U-Th)/He thermochronology that allows for single spot dating of individual crystals, and has already been applied to monazite and zircon (U-Th)/He dating (Boyce et al., 2006; 2009; Vermeesch et al., 2012).

As outlined above and summarized in Table 1 many mineral species are suitable for more than one analytical method and, thus, different geochemical and/or geochronological parameters can be determined on a single mineral grain. In this way it is possible to perform high-T and low-T geochronology on the same single crystal. This approach is called double dating or triple dating. The combination allows for determining both formation ages and cooling ages of single grains and mark very characteristic populations on formation age vs. cooling age plots (Fig. 2). The approach is especially suited for young sediments in actively eroding tectonic settings. Besides increased discrimination of sources and improved inferences on drainage patterns, a major advantage is the straightforward detection of volcanic contributions which are characterized by identical ages obtained from both methods (Fig. 2). The detection of the presence of volcanic units in the catchment area, being also nicely reflected in bulk sediment composition, is crucial for sediment production studies, because the elevated weathering and erosion rates of loose and highly reactive volcanic ashes in the source areas should be considered for estimation of sediment production.

Regarding zircon double dating, Rahl et al. (2003) and Reiners et al. (2005) combined zircon U-Pb dating with (U-Th)/He thermochronology, while Carter and Moss (1999), Bernet et al. (2006), and Mikes (2008) applied zircon U-Pb geochronology in combination with fission track dating. A combination of low-T techniques as applied by Cox et al. (2010) used FT and (U-Th)/He dating on the same detrital apatite crystals. The combination of low-T and high-T dating methods is not only restricted to zircon. Recent progress has been made with respect to apatite triple dating (U-Pb, FT, and (U-Th)/He) (Danisik et al., 2010) and this technique has also been applied to detrital apatite (Carrapa et al., 2009). It is straightforward to predict an increasing use of multiple dating techniques in future studies trying to unravel drainage patterns and sediment yield in thermally and structurally complex geological settings.

2.2.4. Remarks on the statistical evaluation of single-grain age distributions

The prime outcome of detrital geochronological studies is actually a single-grain age distribution, which can be unimodal or complex in character. The evaluation and comparison of such distributions requires graphical presentation and the identification and description of age components by robust statistical methods.

The first issue in evaluating single-grain age distributions is the selection method of the dated grains (i.e. are the selected grains representative for the dated sedimentary formation?). Theoretically the sampling should be unbiased and the grain age distribution should represent the entire population of the dated mineral phase from the investigated sample. During sample preparation, however, grain-size separation and even magnetic separation procedures are prone to some fractionation effect in case of, for instance, zircon, titanite or monazite grains (Sircombe and Stern, 2002; Lawrence et al., 2011). The potential operator bias due to subjective grain selection is thought to have an even stronger influence. The intrinsic expectation of an immaculate clear character of crystals for (U-Th)/He geochronology definitely excludes the dating of fractions derived from lithologies containing milky apatite or very thin zircon grains. A similar, but less pronounced bias appears at the selection of crystals for FT and U-Pb dating.

The age components of detrital single grain age distributions have generally higher uncertainty compared to classical multi-aliquot ages determined on igneous rocks, because the desired unbiased grain selection requires dating of less ideal grains, which would not be
considered in case of basement studies. Furthermore, the ages must be evaluated without knowledge on the individual paragenetic context (e.g. Allaz et al., 2011). Therefore, detrital U–Pb age distributions, for instance, often have comparatively high percentage of discordant ages and also higher degrees of discordance. This implies that a significant proportion of the grains may show $^{206}\text{Pb}/^{238}\text{U}$ or $^{207}\text{Pb}/^{206}\text{Pb}$ ages between two thermal events in the source area and thus, carries only very limited geological meaning although analytical precision might be high.

In case of fission track ages the generally very low number of radioactive decay events (typically 5 to 100 spontaneous tracks per grain counted) primarily determines the uncertainty. Compared to U–Pb ages single-grain FT ages have huge uncertainty and the age components extracted from the measured age distributions have wider scatter, illustrated by wide and often diffuse ranges in the probability density plots. Therefore, the age resolution of the FT method is limited. This is especially true for apatite FT ages, because apatite crystals have typically order(s) of magnitude less uranium than zircon, implying

![Diagram](image)

**Fig. 2.** Double dating. **a:** Principle of double dating by combined low-T and high-T geochronology performed on individual grains, allowing for characterization of source terrains according to formation and cooling data for each single grain. This schematic example demonstrates some of the major age clusters documented in Central European crustal rocks and Phanerozoic sediments (gray fields). The dominant magmatic sources are Cadomian and Variscan intrusive rocks. Later the European crust (besides the Alps) experienced thermal overprint mainly during Jurassic rifting and in the Late Cretaceous, thus low-temperature cooling ages cluster around these times (Timar-Geng et al., 2004). Note that unreset volcanic events are well defined because high-T and low-T geochronology yield similar ages (i.e. plot on the 1:1 line). **b:** An example for zircon double dating from the Tertiary flysch of the Dinarides, where the source of the siliciclastic detritus is strongly debated. Double dating allows for significant constraints on the complex provenance history that could not be obtained by single dating techniques. For instance, (i) Late Cretaceous volcanism can be discriminated from Late Cretaceous cooling, and (ii) erosion of Permian and Early Triassic igneous rocks reveals a clear distinction regarding Late Cretaceous cooling that is only recorded in zircons related to Permian magmatism. Data from Mikes, (2008).
sizes do not allow for a robust detection of small age components
grains should be dated (Vermeesch, 2004). Mass balance considerations
PopShare, BayesMixQt and RadialPlotter (Brandon, 1992; Dunkl and
Several computational tools are available for this purpose, e.g. BinomFit,
only 40 to 60, rarely 100
of deposition, provided that burial temperature has not reached Tc.
contrast, detrital
method, around a hundred grains per sample are dated typically. In
detrital
–Pb geochronology, which is about the fastest and cheapest
around a hundred grains per sample are dated typically. In
contrast, detrital fission track thermochronological data usually contain
only 40 to 60, rarely 100 fission track ages per sample. Such low sample
sizes do not allow for a robust detection of small age components
(Vermeesch, 2004; Stewart and Brandon, 2004; Andersen, 2005).
For instance, to exclude at the 95% confidence level that a component
comprising more than 5% of the total age distribution is missed, at least 117
grains should be dated (Vermeesch, 2004). Mass balance considerations
based on single-grain age distributions are, beside geological issues
such as contrasting mineral modal abundances in source rocks and frac-
tionation during sediment transport, fraught with statistical problems
especially regarding small (~10%) age components (Andersen, 2005).
Among others Galbraith and Green (1990), Galbraith and Laslett (1993)
and Sambridge and Compston (1994) published considerations and pro-
cedures on the identification of age components and their parameters.
Several computational tools are available for this purpose, e.g. BinomFit,
PopShare, BayesMixQt and RadialPlotter (Brandon, 1992; Dunkl and Székely, 2002; Jasra et al., 2006; Vermeesch, 2009, respectively).
The youngest component of a grain-age distribution carries very
important geological information. First of all, the youngest cooling or
 crystallization ages in the sedimentary record mark the maximum age
of deposition, provided that burial temperature has not reached Tc.
Given fossil-poor continental deposits such as coarse-grained red beds
or slightly metamorphosed monotonous sedimentary sequences this
approach might yield the only chronostratigraphic information
(e.g. Najman et al., 2001; Surpless et al., 2006; Leier et al., 2007).
A second important characteristic of the youngest age component is
related to the so called lag-time concept. The lag time is defined as the
difference between the youngest cooling age component of the sample
and the age of sedimentation (Zeitler et al., 1986). A pragmatic and
widely used method for detection of the youngest age component in fis-
sion track grain age populations is the so called “chi-square age method”
(Brandon, 1992), in which the youngest population can be isolated by
the chi-square test. The chi-square age is defined as the “age of the largest
group of young grains that still retains chi-square probability greater than 1%
per cent”.
If the stratigraphic age of the dated sample is known and the youngest
age component is relatively close to the stratigraphic age, further if the
dated grains of the youngest component are not volcanic, then it is possible
to use the contrast of ages to describe geodynamic aspects of exhumation
processes in the source areas. The lag time expresses the apparent
rate of cooling and exhumation of the corresponding source units of the
sediment for the temperature range of the applied thermochronometer
(e.g. Bernet and Garver, 2005). For details of the lag-time concept as
well as dynamic aspects of short and long lag times and their evolution
through time we refer to Section 4.1.
It is important to note that for the identification of the youngest
geo logical meaningful age signal in detrital sediment the use of the
youngest single-grain age is not a feasible way. The result of any single
grain dating approach, even in well-defined short-lived volcanic units,
is an age distribution where approximately one half of the dated grains
is younger than the mean of the distribution (that is usually considered
to reflect the correct age of the respective event; Fig. 4). The youngest
single-grain age is always the most extreme member of the distribution.
The difference of the youngest age and the mean of the youngest age
component, i.e. the error related to the erroneous use of the youngest

Fig. 3. The principle of presenting single grain ages with variable uncertainty on a ra-
dial plot (Galbraith and Green, 1990). Such plots express the precision of the individual
grain ages calculated by the Poisson uncertainty from the number of tracks counted.
In this example the “red” crystal contains comparatively few tracks, thus the counting
uncertainty is as high as 40% relative error. The “blue” crystal contains more tracks, thus
counting statistics indicates smaller relative error of ca. 15%. The errors of the single
grain data can be visualized in million years by the intersection of the radial age
array and the dashed lines running from the origin to the extremes of the 2 sigma un-
certainty bars. These vertical bars are uniform for all data points of a sample, but the
distance of the data points from the origin (= their error) is variable, resulting in indi-
vidual error ranges for each grain. Note that in this kind of data presentation the age
scale is not linear.

lower track density and poor counting statistics. Thus correct and in-
formative presentation of single-grain FT ages requires showing both
the ages and the individual errors of the data. For this purpose the so-called radial plots are recommended (Fig. 3).
The size of a data set (i.e. the number of dated grains generated
from a sample) has a cardinal role for the resolution of detrital geo-
chronology. Ideally age data from several hundreds of grains should
be measured, but this is usually not feasible due to high costs, and
sometimes even the size and mineral concentration of the sample
(e.g. drilling cores) does not allow a high number of analyses. In detrital
zircon U–Pb geochronology, which is about the fastest and cheapest
method, around a hundred grains per sample are dated typically. In
contrast, detrital fission track thermochronological data usually contain
only 40 to 60, rarely 100 fission track ages per sample. Such low sample
sizes do not allow for a robust detection of small age components
(Vermeesch, 2004; Stewart and Brandon, 2004; Andersen, 2005).
For instance, to exclude at the 95% confidence level that a component
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Given fossil-poor continental deposits such as coarse-grained red beds
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per cent”.
If the stratigraphic age of the dated sample is known and the youngest
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to use the contrast of ages to describe geodynamic aspects of exhumation
processes in the source areas. The lag time expresses the apparent
rate of cooling and exhumation of the corresponding source units of the
sediment for the temperature range of the applied thermochronometer
(e.g. Bernet and Garver, 2005). For details of the lag-time concept as
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It is important to note that for the identification of the youngest
geo logical meaningful age signal in detrital sediment the use of the
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grain dating approach, even in well-defined short-lived volcanic units,
is an age distribution where approximately one half of the dated grains
is younger than the mean of the distribution (that is usually considered
to reflect the correct age of the respective event; Fig. 4). The youngest
single-grain age is always the most extreme member of the distribution.
The difference of the youngest age and the mean of the youngest age
component, i.e. the error related to the erroneous use of the youngest

Fig. 4. Two age distributions with high number of measured grains demonstrating the
uselessness of the “youngest age” concept for lag-time purposes or for determining
minimum stratigraphic ages. a): Binned age plot shows the empirical distribution of
403 single-grain zircon fission track ages determined on the well studied Fish Canyon
tuff. The mean of the entire population is close to the known age of the volcanic eruption,
but the youngest age is ca. 12 Ma younger. b): Single-grain U–Pb age distribution deter-
mined on an igneous formation from Central Tibet reveals considerably smaller (relative)
scatter compared to ZFT or AFT ages (data from Haider et al. in prep). However, even such
precise U–Pb ages have remarkable spread and the youngest age can be significantly
younger than the geological meaningful mean of the entire population.
single-grain age approach, depends on the applied chronological method, on the scatter of the given age component, and on the number of dated grains.

3. Sediment modification during weathering, transport, and deposition

D detrital mineral spectra obviously cannot be considered as a one-to-one image of the mineral composition of the source rocks. Several processes modify sediment characteristics including chemical weathering, mechanical comminution and abrasion during transport, hydrodynamic sorting, as well as the specific conditions of the depositional environment (e.g., Johnsson, 1993; Weltje and von Eynatten, 2004). These processes may cause substantial changes in sediment composition, especially affecting the ratios of relatively unstable to stable minerals as well as intra-sample variability across grain-size grades. The degree of modification in a given geologic setting depends on individual mineral grain properties such as size, shape, density, breakage, hardness, and chemical resistivity under the relevant environmental conditions.

Compositional variability related to hydrodynamics follows principal physical rules of settling equivalence and selective entrainment (e.g. Rubey, 1933; Slingerland, 1977) and their theoretical effects on sediment composition of a specific grain size fraction can be precisely modeled (Garzanti et al., 2009). However, several factors may obscure these calculations including transport mechanism, transporting medium, complex grain shapes, mineral intergrowths, uncertainty in mineral densities, vegetation, entrainment related to bed roughness, etc. (Reid and Frostick, 1985; Morton and Hallsworth, 1999; Garzanti et al., 2008). Mechanical abrasion related to hardness and cleavage of minerals generally appears to be negligible in modifying heavy mineral proportions (see review in Morton and Hallsworth, 1999). This is corroborated by the observation of positive correlation between the average lifetime of detrital grains and their chemical durability, while no correlation was observed between lifetime and mechanical durability, i.e. hardness (Kowalewski and Rimstidt, 2003). Chemical abrasion, i.e. chemical weathering, is well known to effectively modify the ratios of chemically unstable to stable minerals (e.g. Mange and Maurer, 1991; Morton and Hallsworth, 1999). Using ratios of mineral pairs that behave hydrodynamically equivalent (Morton and Hallsworth, 1994), but show contrasting stability against chemical weathering such as apatite and tourmaline are best suited to unravel chemical alteration at the source and/or on transit (Morton and Johnsson, 1993).

Other ratios such as garnet vs. zircon are used to detect increasing chemical modification with sediment burial (Morton and Hallsworth, 1999), while ratios of (ultra)stable and hydrodynamically equivalent minerals such as zircon and rutile can be considered as not being modified by sedimentary and diagenetic processes, i.e. they reflect the original proportions in the source rock(s).

The application of single-grain methods in provenance analysis principally assumes that differential fractionation of grains from a single mineral phase (or group) is negligible (Morton, 1991). This is because the methods focus on variability within a mineral phase or group that is considered to be “homogeneous” with respect to fractionation by mechanical and chemical processes in the sedimentary system. The properties and variability of the respective detrital mineral group are thus considered as directly reflecting source rock characteristics (chemistry, age, proportions of subgroups, etc.) without significant modification by earth surface and/or diagenetic processes. This assumption, however, is not always justified. Strong density contrasts known for some solid solutions series such as garnet, epidote, and pyroxene group minerals may cause significant hydrodynamic enrichment of some endmember-phases in certain grain-size fractions or layers of, for instance, beach placers. Moreover, inclusions of various kinds may add to the density contrast between grains of the same mineral phase. Some solid solution endmembers are also known for contrasting behavior with respect to chemical weathering under surface or diagenetic conditions. Ca-rich garnets, for instance, are less stable than Ca-poor garnets during diagenesis, and this may lead to decreasing diversity in garnet suites with increasing burial (Morton and Hallsworth, 2007). These authors also infer that calcic amphibole is less stable than sodic amphibole as previously suggested by Pettijohn (1941).

More importantly, there might be a direct relationship between grain size and composition or age information, i.e. specific mineral phases may show systematically contrasting grain-size distribution in the same or in different source rocks. Ultimately, the grain size distribution in the source rocks controls the availability of specific mineral grain sizes in the sediment (Morton and Hallsworth, 1999). This is, for instance, the case for tourmaline that usually occurs with larger size in granitoids and associated late stage differentiates (i.e. pegmatites) compared to metapelitic rocks. In a study of modern detrital tourmaline from Cheyenne River and some small tributaries draining the southern Black Hills in South Dakota (US) (Viator, 2003) it was found that tourmaline nicely reflects parent lithology according to the scheme introduced by Henry and Guidotti (1985); see Section 2.1.1. However, provenance information is strongly biased by grain size, i.e. very fine to fine sands (the fractions that are mostly used for classical heavy mineral analysis) are dominated by metamorphic tourmaline while medium and coarse sands are dominated by granitic tourmaline (Fig. 5; Viator, 2003). Although demonstrated so far for such proximal setting only, this effect may have significantly contributed to the predominance of metamorphic tourmaline reported from various settings (e.g. von Eynatten and Gaupp, 1999; Preston et al., 2002; Mange and Morton, 2007; Mikea et al., 2008; von Eynatten et al., 2008; Wotzlaw et al., 2011), and should be considered more carefully as most heavy mineral and single grain studies focus on the 63–125 μm or 63–250 μm size fractions.

A similar complication in discriminating and interpreting sediment provenance using detrital mineral geochemistry could be expected when dealing with some other phases, for instance epidote group minerals (e.g. Yokohama et al., 1990; Spiegel et al. 2002). Epidote and related minerals (zoisite, clinozoisite) are typically formed through plagioclase replacement during low-grade metamorphism or in the epidote–amphibolite facies in metamorphic rocks. These minerals potentially reproduce the plagioclase grain-size distribution which is preferentially coarse in plutonic rocks and some intermediate volcanics and, usually, relatively fine-grained in basalts and their respective greenschist facies equivalents (note that in amphibolites epidote may be coarse as well). Like for tourmaline such inherited grain-size relations may cause considerable bias in provenance analysis of several mineral phases that are not yet fully explored.

For rutile, such grain size control on composition was not observed in a systematic study by von Eynatten et al. (2005). These authors compared rutile from two detrital grain size fractions (fine and very fine sand) from seven localities in the Central Alps of Switzerland.
the Erzgebirge in Germany, as well as Paleozoic rocks and Pleistocene glacial sediment from Upstate New York. The trace element concentration in rutile does not systematically discriminate between the two grain size fractions. The strong variability observed between localities was clearly dominated by different source rocks (Zack et al., 2004b; Triebold et al., 2007; see Section 2.1.2).

Zircon has not yet been evaluated with respect to grain size vs. trace element relations, but, recently, Lawrence et al. (2011) reported evidence for systematic grain-size influence on detrital U–Pb ages due to hydrodynamic fractionation. They studied modern sediment from several sites along the Amazon river basin and demonstrated empirically that (i) zircon grain size is positively correlated to the grain size distribution of the host sediment sample, and (ii) zircon U–Pb ages show highly significant negative correlation with zircon grain size, i.e. smaller grains tend to have older ages (Lawrence et al., 2011). Such correlation could be observed both on the drainage basin scale as well as for a single bedform, in this case a 20 m long low-amplitude dune from scroll bar deposits (Fig. 6). From the latter samples were taken at five places along a transect normal to the dune crest from the foreset toe via the crest to the upstream end of the dune (Lawrence et al., 2011). Even at this small scale, some (statistically verified) age components occur in certain samples with proportions up to ~20% but are absent in neighboring samples indicating real contrast according to the criteria given by Vermeesch (2004). The ratio of, for instance, pre-Grenvillian (>1.3 Ga) to young zircons (in this case <400 Ma) varies in this example from ~6 down to <1 at the bedform scale (Fig. 6). The study by Lawrence et al. (2011) underlines the strong need for careful recording of both sample and single grain physical properties.

4. Linking single-grain information to sediment flux

Weltje and von Eynatten (2004) stated that “the full potential of single-grain techniques will be realized only if their results can be firmly connected to the bulk mass transfer from the source area to the sedimentary basin, i.e., the parent-rock mass corresponding to a single grain must be known”. Since then significant progress has been made in the analytical techniques towards new tools, higher precision and faster sample throughput (see Table 1 and Section 2). This technical advancement has been applied in numerous case studies deciphering detailed source rock characteristics (e.g. Keulen et al., 2009; Hietpas et al., 2010; Okay et al., 2011; Tsikouras et al., 2011). The problem of relating the highly sophisticated provenance information obtained from single grains to drainage and basin wide sediment budget calculations, however, has not yet been solved in a comprehensive and satisfying way. First and foremost this is because (i) sediment compositional characteristics a priori only allow for assessing relative contributions from different sources (e.g. Palomares and Arribas, 1993; Weltje and Prins, 2003), and (ii) modal abundances of (accessory) mineral phases in the source rocks, that are essential for budget calculations based on single detrital grains, are highly variable and usually unknown. Parts of the uncertainty may be avoided or reduced by detrital single-grain thermochronology. These techniques can be used for estimating rates of sediment generating processes (e.g. Huntington and Hodges, 2006; Brewer et al., 2006; Rahi et al., 2007; see Section 4.1).

Absolute values on mass transfer, i.e. sediment budget calculations, require robust sediment volume estimates in combination with precise stratigraphic control (e.g. Ensele et al., 1996; Kuhlemann, 2000). Furthermore, the individual masses per time slice, obtained after corrections for porosity and density, need to be partitioned to the respective source regions. Uncertainties in this approach are manifold, and include problems in estimating suspended and dissolved load (relative to bedload), imprecise chronostatigraphic control and arguable source-area allocation, as well as basin inversion and sediment cannibalism, i.e. recycling (see Hinderer, 2012, for a current review).

Apart from either very small drainages or large homogenous source areas, partitioning of the detrital material to the respective source areas requires unmixing of sediment derived from contrasting sources. If the sources are known or could be reasonably well constrained, endmember modeling can be applied, i.e. the proportion of each endmember that have contributed to sample composition is quantified (e.g. Weltje, 1997). Applications of this approach to fine-grained sediments typically used grain size data, geochemical data or combinations thereof to decipher, for instance, climate controlled variation of fluvial versus eolian input into shelf seas (e.g. Stuut et al., 2002) or sediment origin from icebergs and/or ice- sea versus ocean bottom currents (e.g. Prins et al., 2002).

Endmember unmixing thus provides proportions of sediment derived from distinct sources (and/or transported by a certain process). In combination with further absolute information on sediment mass, sediment budget calculations can be performed. This additional information might be mass accumulation rates inferred from seismic lines and borehole data (e.g. Brommer et al., 2009; Weltje and Brommer, 2011), or sediment volumes or masses derived from reservoirs in fluvial systems like Brahmaputra, Indus, or Nile (Garzanti et al., 2005, 2006a). The latter studies used petrographic data of very fine to medium sand fractions from tributaries as well as from the main river course for mixture modeling. All these quite detailed and precise studies focus on modern or post-LGM sediments. Inferring sediment budget data for longer timescales or some time slices in the geological past obviously suffers from higher uncertainty, and in general getting more and more arguable the older the sediments are (e.g. Kuhlemann et al., 2001; Hinderer, 2012). In contrast relative data on the contribution of different source rocks or areas are not necessarily obscured when going deeper into geological time (see Section 4.2).

4.1. Rates of mass transfer inferred from detrital thermochronology

Thermochronology-based estimations of erosion rates use the above introduced lag time concept for the numerical expression of the rate of exhumation (Fig. 7). A short lag time generally indicates rapid exhumation in the source area while a long lag time is mostly considered to reflect slow exhumation (Fig. 7a). For lag time calculation sedimentation age is subtracted from the isolated youngest age component obtained from

![Fig. 6](image-url) Variation in ratios of zircon U–Pb age groups vs. grain size from five samples A to E from a single 20 m long low-amplitude subaerial dune bedform in the lower reaches of the Amazons river (data and inset figure are from Lawrence et al., 2011). All samples are dominated by well-sorted fine-grained sand but represent different hydrodynamic microenvironment along the dune body. The ratio of the proportions of the oldest age group (>1.3 Ga) over the youngest age group (<400 Ma) may vary by up to a factor of 7 (sample C vs. A), and is higher for the slightly fine-grained samples, consistent with the overall observation along the Amazons river (Lawrence et al., 2011). The other two ratios involve the most prominent Grenvillian age group and still vary by up to a factor of >3, although variation in grain size is small and usual sampling strategies would consider the material as homogeneous.
the age distribution of an arenite sample. Alternatively, multi-method cooling ages obtained from a single pebble from a coarse-grained layer may be used. The information gained by this approach is primarily a time period (i.e. lag time) and temperature information corresponding to \( T_c \) of the applied thermochronological method. To transfer this information on cooling \([°C/My]\) into robust constraints on erosion rate \([\text{mm/year or km/My}]\) or sediment yield \([\text{t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}]\) or absolute masses of sediment per time slice, several assumptions have to be made:

(i) The geothermal gradient \([°C/km]\) is a multiplication factor that is used for inferring eroded thickness from thermochronological data which only provide time and temperature constraints. Estimating paleo-geothermal gradients introduces significant uncertainty into the calculation of the eroded masses. Significant spatial and temporal variations in the gradient may occur, for instance, throughout the development of an orogenic nappe pile. Magmatic underplating or intense volcanism can also have a high and spatially variable effect on geothermal state of the crust. In relatively well-known geologic settings the paleo-geothermal gradient may be computed from the bulk petrophysical parameters from the exhuming rock masses and from the cooling rate by iterations (Rahl et al., 2007).

(ii) Calculations of sediment yield from erosion rates (eroded thickness per time) require sound estimates of sediment porosity and material density. Furthermore, to relate absolute volumes or masses of sediment deposited in a basin to sediment yield, the size of the drainage basin must be known or reasonably estimated (Hinderer, 2012). Obviously, these estimates will suffer from higher uncertainty when going back in the geological past.

(iii) All these basically straightforward calculations require general assumption of a continuous exhumation process. If this is not the case, i.e. exhumation took place in abrupt pulses, the long-term average cooling rate (that is what the thermochronological data actually deliver) provides a coarse estimation only.

(iv) The depth of erosion must have reached the reset zone of the used thermochronometer; otherwise dating will yield only older ages reflecting previous tectonic events (Rahl et al., 2007), and calculations of lag time, exhumation rate, rate of erosion, etc. would be meaningless.

(v) The mineral of the chosen thermochronometer has to be representative for the eroded rock units. This is not necessarily the case and should be supported by independent (provenance) information.

A fundamental prerequisite for sediment budget calculations based on detrital thermochronology is information on the style of removal of the uppermost layer of the crust, i.e. the process that triggers exhumation. In principal, tectonic denudation and erosive denudation have to be distinguished (e.g. Reiners and Brandon, 2006). If crustal thinning or normal faulting contributes to exhumation, the former cover of an exhuming rock unit does not entirely transform to detrital material, because part of it will simply slip away. Tectonic denudation can generate very high cooling rates (e.g. exhumation of metamorphic core complexes) resulting in pretty young ages and short lag times, but these data are misleading with respect to quantification of erosion. Instead of generating high amounts of sediment, tectonic denudation may even reduce relief and cause a drop in sediment generation (e.g. Kuhlemann et al., 2001). Erosive denudation (i.e. erosion) refers to exclusive removal of the upper layer of the crust by mechanical and chemical alteration processes at the surface followed by down-slope transport of material in the respective drainage system. Only in this case is the exhumed cover rock quantitatively transferred to the sediment. Consequently, erosion can be quantified based on detrital thermochronology only if it could be demonstrated that erosive denudation forms the predominant exhumation process in the source area.

Profound evaluation of lag time regarding the quantification of erosion requires investigation of lag time through stratigraphic columns, i.e. the variability of lag time with geologic time is crucial for understanding (e.g. Bernet and Garver, 2005; Rahl et al., 2007). Deciphering the dynamics of an orogen involving complex structural evolution, volcanism, and/or sediment recycling from the orogenic wedge, requires tracking the temporal change in lag time not only to observe absolute values but to identify the stationary or moving character of age components (e.g. Malusà et al., 2011). Old stationary age components, for instance, are not relevant for determining timing and rates of exhumation and erosion, while young moving age components may reflect source area dynamics quite precisely (for some possible scenarios see Fig. 8).

Detrital thermochronological studies aiming at unraveling near surface processes are dominantly based on apatite and zircon FT or \((U-\text{Th})/\text{He}\) thermochronology ranging in \( T_c \) from approx. 60 to 280 °C. Given the lowest closure temperature (AHe), thermochronological data typically express subvertical movement in the depth of at least 1.5 km below the surface. Note that this subsurface cooling period necessarily predates the transformation of the source rocks to the sediment that occurs later at the earth surface.

4.2. Relative proportions of sediment flux

Approaches using bulk petrographic-mineralogical data obviously have high potential for detailed source-rock characterization (beyond discrimination), and are intimately linked to the plenteude of single-grain techniques described in Section 2. The major drawback of the quantitative bulk sediment petrographic approach (i.e. point-counting), besides possible sediment modification on transit (see Section 3), is the time-
Fig. 8. Conceptional sketch showing exemplary relations of single-grain age components vs. stratigraphic age (compiled after Bernet et al., 2006 and Malusà et al., 2011). Only if moving peaks (green lines; in contrast to stationary peaks shown with dashed blue lines) are well defined the data can be used to infer cooling, exhumation or erosion rates from lag time of detrital age populations. Dashed gray lines contour lag time (i.e. mean of age population minus stratigraphic age). 1: Old stationary peak reflecting previous tectonic phase (e.g. detrital U/Pb ages recording intrusions or metamorphic processes); there may be several peaks of this kind in a detrital age spectra. 2: Young stationary peak reflecting volcanic event (e.g. detrital zircon U/Pb or apatite or zircon low-T chronometer ages from young volcanic sources). 3: Young stationary peak (3a) that evolves into moving peak with constant lag time. This scenario includes data from different techniques, with 3b reflecting mineral-method pair with lower Tc-range compared to 3c (e.g. detrital apatite and zircon FT data, respectively, derived from moderately to slowly exhuming hinterland including igneous complexes). 4: Complex moving peak reflecting strongly decreasing lag time in the lower part peaking at rather short lag time in the middle part, and upsection increasing lag-time (e.g. detrital apatite FT data related to rapidly exhuming and eroding orogens with distinct climax in cooling/exhumation rates).

Consuming process of data generation, especially when several grain-size classes are considered to cover large parts of the entire grain size spectrum. Data generation, however, can be accelerated by 1 to 2 orders of magnitude through applying automated data acquisition technologies using scanning electron microscope equipped with some spectrometer and computer-controlled grain recognition and phase determination (such as CSSEM, Quemscan®, Mineral Liberation Analysis), allowing for comprehensive analysis of detrital mineral characteristics (e.g. modal abundance, major element composition, size, and shape; e.g. Bernstein et al., 2008; Keulen et al., 2009; Haberlah et al., 2010; Tsikouras et al., 2011). For precise and fast phase recognition even in the silt range Raman spectroscopy is another very useful tool (Andò et al., 2011). The advantages of all these methods are (i) extremely fast data generation (the producers of Quemscan®, for instance, promise throughput of > 10,000 grains per minute), (ii) reduction of subjectivity in data acquisition by different operators, and (iii) the extension of petrographically obtainable data to the silt range where classical optical identification is hindered. Applying these methods, specific heavy mineral ratios that are thought to be transport invariant and/or reflect sediment alteration processes (e.g., apatite/tourmaline, rutile/zircon, garnet/zircon, monazite/zircon, chrome-spinel/zircon; Morton and Hallsworth, 1994) will be determined very quickly and with high precision. Linking these kinds of ratios to bulk petrography (e.g. quartz and feldspar contents) as well as to the very precise single-grain information appears to be a very rewarding approach for future studies that need reliable estimates of the relative contributions of source rocks to understand the sediment flux from source to sink.

As most single grain geochronologic studies rely on zircon only, problems arise from the fact that some major zircon-free lithologies such as carbonates and basalt, metasomatic, or ultrabasic rocks are not represented at all in the detrital age spectra. Thus, provenance interpretation based on zircon alone may lead to significant bias in provenance interpretation (e.g. Spiegel et al., 2004). Even if all source rocks contain zircon, contrasting concentration, crystal size, and/or quality (e.g., variable susceptibility to disintegrate during transport; Sláma and Kössler, 2012) of zircon from different rocks preclude the use of the relative proportions of zircon age components from different samples to infer the relative contribution of different sources, unless modal abundance and size of the zircon in the host rocks is known or could be reasonably estimated (see also Fig. 6). This holds true for any mineral and data type, for instance, source rock discrimination based on tourmaline chemistry faces similar shortcomings (Fig. 5). Investigating mineral pairs (see above) may significantly reduce these problems including the under-representation of younger events in zircon U–Pb geochronology (e.g. Hietpas et al., 2010). The latter authors used combined monazite–zircon U–Th–Pb geochronology but this mineral pair is considered less informative compared to zircon–rutile with respect to both low-T cooling and petrogenetic characterization of the source area(s).

Among several mineral pairs, zircon and rutile are considered unique as they form under very different petrologic conditions. In contrast, zircon and rutile behave very similarly within the sedimentary cycle due to their high chemical and mechanical stability and lack of significant hydrodynamic fractionation due to their similar size, shape and density (Morton and Hallsworth, 1994). That means their occurrence and proportions should largely reflect their ultimate sources. Zircon is the most frequently used mineral in single grain analysis, especially regarding chronology, and may derive from almost any major source rock (except carbonates and (meta)basic to ultrabasic rocks). Regarding metamorphic source rocks (including metabasic rocks), rutile is considered a hitherto unique mineral phase for extracting a wide range of geologic information from single detrital minerals without specific knowledge of source rock mineral paragenesis. It allows for discriminating source rock lithology as well as calculating the metamorphic thermal conditions of mineral growth and is well suited for medium (U–Pb) and low temperature [(U–Th)/He] thermochronology (see Sections 2.1.2, 2.2.1, and 2.2.3). A major contrast is that zircon usually records several orogenic cycles, while rutile records mainly the latest orogeny (Fig. 9). In fact, zircon may even miss important geodynamic events because (i) the exposed rocks of the latest orogeny may have not reached granulite-facies metamorphism or partial anatexis to produce new overgrowth pairs (see above) may significantly reduce these problems including the under-representation of younger events in zircon U–Pb geochronology but this mineral pair is considered less informative compared to zircon–rutile with respect to both low-T cooling and petrogenetic characterization of the source area(s).

Like for zircon and rutile, the advantage of applying a multi-method approach can be demonstrated for many other cases, minerals, and detrital mineral pairs or associations. As outlined in Section 2 each of the single-grain methods has its individual drawbacks that are partly intrinsic and cannot be resolved based on the respective method alone. For instance, systematic bias in zircon U–Pb ages (e.g. failure to record young orogenic events) or zircon FT-ages towards younger ages cannot be compensated for by simply dating more grains. Even enhanced methodical protocols (e.g. several mounts in case of ZFT, or preferred dating of cores and rims in case of zircon U–Pb; Andersen, 2005, see above) will not allow for measuring a representative sample for the entire zircon suite. This further underlines the need for multi method approaches, that could be either combinations of methods applied to the same mineral phase
(e.g. double dating or geochronology combined with trace element systematics), or methods on different mineral phases. The latter has the additional advantage wherein changes in mineral ratios (see above) and the contrasting behavior of the minerals during source-rock metamorphism or later in the sedimentary cycle can be considered properly.

We have shown that in many cases combined information from one mineral group (geochemistry, high-T chronology, and low-T chronology) strongly increases source area understanding. Regarding source-rock lithology the discrimination of metamorphic vs. igneous rocks is fundamental. This is best done by the occurrence of key index minerals and mineral associations. Because these may become obscured during earth surface processes, stable minerals provide prominent methods such as tourmaline major element composition and zircon Th/U ratios to discriminate metamorphic vs. igneous rock origin. Other single grain techniques are available but have several limitations that need additional information before applying them. If the distinction of metamorphic vs. magmatic origin is successful, several further methods are suggested for more sophisticated characterization of the source rocks, for instance, the degree of metamorphism or magmatic differentiation and their variation through space and time. We have highlighted several of these techniques, among them Fe-Ti-oxide structure and major element composition, trace element and REE concentration in pyroxene and amphibole, rutile Cr-Nb systematics, Zr-in-rutile thermometry, epidote trace element concentration and Nd isotopes, and phengite geobarometry, as well as garnet major and trace element composition.

5. Summary and outlook

We have reviewed the ever increasing number of analytical methods to extract information from single detrital grains in order to characterize the nature and chronology of their source rocks. Regarding source-rock lithology the discrimination of metamorphic vs. igneous rocks is fundamental. This is best done by the occurrence of key index minerals and mineral associations. Because these may become obscured during earth surface processes, stable minerals provide prominent methods such as tourmaline major element composition and zircon Th/U ratios to discriminate metamorphic vs. igneous rock origin. Other single grain techniques are available but have several limitations that need additional information before applying them. If the distinction of metamorphic vs. magmatic origin is successful, several further methods are suggested for more sophisticated characterization of the source rocks, for instance, the degree of metamorphism or magmatic differentiation and their variation through space and time. We have highlighted several of these techniques, among them Fe-Ti-oxide structure and major element composition, trace element and REE concentration in pyroxene and amphibole, rutile Cr-Nb systematics, Zr-in-rutile thermometry, epidote trace element concentration and Nd isotopes, and phengite geobarometry, as well as garnet major and trace element composition.
Fig. 10. Schematic compilation of common scenarios in detrital geochronology performed along sedimentary sections. Age distributions and actual age components deliver useful information, however, some additional information on source rock lithology (petrologic proxies, cases I. to III.) is essential, as interpretation will strongly depend on whether the situation shows constant petrologic proxies or distinct breaks or gradual trends along with changes in detrital single-grain chronology. It should be noted that such petrologic proxies (e.g. grain-type or heavy mineral ratios, single-grain mineral chemistry) are mostly easier to obtain, and usually available at more stratigraphic levels than detrital geochronology. Yellow bars represent the age of sedimentation, open circles indicate sample density for defining trends in petrologic proxies. All of the methods mentioned in the text and Table 1 could be used as petrologic proxies, however, some especially useful ones are listed for some of the cases. Scenarios 1 to 3 focus on multi-component zircon U–Pb age distributions where the ages typically reflect mineral crystallization, while scenarios 4 and 5 are designed for low-temperature thermochronometers like detrital ZFT, AFT and (U–Th)/He methods. Scenarios and cases are not intended to cover all possibilities but to highlight typical situations and possible interpretations.
Beyond source grain lithology geochemical analysis of single grains allows for precise dating of geodynamic events and processes in the source area. The result of any geochemical survey of single detrital grains is age distribution, independent of whether high-T or low-T techniques are applied. Careful statistical handling of these distributions is inevitable to avoid or reduce fundamental problems such as sampling bias, sample size, detection of age components from complex distributions, calculation of errors, etc. The youngest dated grain is considered geologically meaningless. The youngest age component, however, is of special importance and intimately linked to the age concept that forms the base for estimating exhumation and erosion rates from detrital thermochronology. Recent developments of great interest for detrital geochronology include rutile U–Pb dating, (U–Th)/He thermochronometry of additional phases (e.g. titanite, monazite, rutile) to overcome the restriction to apatite and/or zircon bearing lithologies, as well as any kind of double or triple dating to extract both high-T and low-T thermochronological information from the very same detrital grains.

Linking single grain petrologic and geochemical information to sediment flux is mainly based on two independent approaches. First, detrital grain geochemical data are used to calculate exhumation and erosion rates in the source areas. This approach has several requirements; among them is the distinction between erosive and tectonic denudation in the source area as well as sound assessment of the (paleo-)geothermal gradient. If applied properly lateral and temporal variations in erosion rates or sediment yield can be established. The second approach relies on sediment composition and itself delivers only relative proportions of sediment flux. As bulk sediment composition is modified under earth surface conditions, only ratios of minerals should be considered that behave similar during weathering and/or transport. Ideally suited are mineral pairs where the two phases occur in contrasting rock types and both allow for extracting significant information on source rock petrology and chronology, such as zircon and rutile, or monazite. Such detailed information on the relative contribution of different well-defined source rocks or areas may be transferred to mass balances, if (i) further single grain information from detrital thermochronology allows for constraining erosion rates, (ii) independent information on sediment mass is available from sedimentary basins or reservoirs, and/or (iii) the modal abundance of the respective mineral phases in the source rocks is available. While (i) can be obtained directly from the investigated sediment samples, completely different methods (e.g. seismic and borehole data) are needed to fulfill criteria (ii). Condition (iii) is strictly applicable to modern settings only, otherwise reasonable estimates are required. Detailed multi-method studies on single detrital grains, where emphasis is placed on the relative proportions of individual source rocks or areas, in combination with either independent information on sediment flux and/or erosion rates derived from single-grain thermochronology, thus give us the opportunity to assess the sediment factory, its processes, controlling mechanisms and overall geologic settings, not only for Neogene to modern case studies, but also when going back in geologic time.

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