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Review article

Chemical compositions of zircon from rare-metal granites of different geochemical affiliations – a review

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Abstract: About 2000 microprobe analyses of zircon were evaluated in order to characterize typical compositions of zircon from common and rare-metal granites of different geotectonic/geochemical affiliations. Generally, zircon is chemically variable at all scales of research. This detailed study shows that the contents of minor elements vary more widely than usually expected from individual analyses. While the Zr/Hf ratio is a reliable indicator of the degree of fractionation of the parent magma, all proposed indicators of the geotectonic position of the source magma, like Y contents or Y/Yb and U/Th values, were found to be merely indicative. Zircon from peraluminous (S-type) granites crystallizes early, is often enriched in P, Al, U, W, Nb and Bi, its (Y+REE)/P values are usually <<1, and the Zr/Hf values mostly evolved from 100 to 10. Zircon in A-type granites is often a relatively late mineral, mostly enriched in HREE and Th, having low Y/Yb and high (Y+REE)/P values, and its Zr/Hf values evolved from 100 to 5. Zircon in peralkaline rocks either crystallizes primarily or results from the transformation of older zirconosilicates. In both cases, it is rich in Y, poor in U and Th, displays high (Y+REE)/P values and Zr/Hf values >50. The effect of the geotectonic environment of crystallization is particularly evident in late, more evolved rocks, while zircons from the early and less fractionated rocks of all geochemical types are similar.

Keywords: zircon, granites, chemistry

Introduction

Zircon is a widely distributed accessory mineral in granitic igneous rocks. For its stability across a broad range of P–T conditions, zircon is a suitable object for various petrological interpretation methods like geochronological studies (Davis et al. 2003), geothermometry (Hanchar & Watson 2003;Watson et al. 2006; Tichomirowa et al. 2019; Shao et al. 2020; Crisp & Berry 2022; Streicher et al. 2023), or source lithology of igneous complexes (Du et al. 2002; Kinny & Maas 2003). Moreover, trace-element assemblages of igneous zircon (Pupin 2000; Hoskin & Ireland 2000; Hanchar & Hoskin 2003; Grimes et al. 2007, 2015; Kirkland et al. 2015) may indicate geotectonic affiliation and the degree of fractionation of magmatic suites. A specific method based on the morphology of zircon crystals allowing interpretation of the crystallization temperature and geochemical affiliation of granite was introduced by Pupin (1980) and further developed, for example, by Broska et al. (1990) and Benisek & Finger (1993).

The routine use of electron probe microanalysis (EPMA) and laser-ablation induction-coupled mass spectrometry (LA ICP-MS) during the last three decades yielded extensive data concerning the chemical composition of zircon; however, most of them dealing with only a single locality, a single mineral deposit, or a single particular type of igneous rock (Černý & Siivola 1980; Broska et al. 1990; Wang et al. 1992, 2000; Uher & Černý 1998; Pettke et al. 2000; Hoskin 2005; Xie et al. 2005; Förster 2006; Pérez-Soba et al. 2007; Zaraisky et al. 2008; De Liz et al. 2009; Van Lichtervelde et al. 2009; Nardi et al. 2012; Kozlik et al. 2016; Viala & Hattori 2021). Comprehensive studies comparing zircon from different igneous rock types are still rather rare (Pupin 2000; Belousova et al. 2002; Hoskin & Schaltegger 2003; Breiter et al. 2014, 2024, 2025; Kirkland et al. 2015).

I decided to contribute to this line of research and summarize about 2000 EPMA of zircon made within different projects during the last 15 years at the EPMA workplaces in Brno and Praha. The available dataset includes mainly typical ore-bearing (or "rare-metal") granite plutons of Variscan Europe from Cornwall across Portugal and France to the Erzgebirge (Germany, Czech Republic), supplemented by Lower Proterozoic "rapakivi"-type plutons from Finland and Brazil, and Jurassic ore-bearing granites of Transbaikalia, Russia. Peralkaline granites are represented by Paleozoic plutons of southern and western Mongolia. Zircon from several types of geochemically less evolved to primitive granitoids from the Bohemian Massif is shown for comparison.

Major aims of this paper are to show: (1) principal differences in chemical compositions of zircon from plutons of different geochemical (geotectonic) affiliations, i.e., peraluminous (S-type), subaluminous (A-type), and peralkaline igneous rocks; (2) different behaviors of some minor elements or their

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ratios in zircon during magmatic evolution of particular plutons of different geochemical affiliations, and (3) the dispersion of zircon data within the same pluton and between plutons of the same geochemical type.

I want to emphasize that in this paper (i) I am trying to define the range of typical element contents in different types of zircon, not taking into account some rare, albeit extreme, contents, and (ii) I deal only with zircon as a mineral (Zr>0.5 apfu); solid solutions with high U, Th and REE (Förster 2006; Breiter et al. 2009) present a different mineralogical problem.

At this point, I want to emphasize that this study focuses on zircon from highly fractionated granites, generally called "rare-metal granites" (RMG), which are characterized, among other, by a high content of Hf and other minor elements, and a low analytical sum. A very limited number of analyses of zircons from common rock types are included only for comparison and to highlight the specific composition of zircon from RMG.

A detailed description of laboratory methods is given in the Electronic Supplement S1, brief geological characteristic of studied plutons in the Electronic Supplement S2. The peraluminosity/peralkalinity and the degree of geochemical fractionation in studied plutons are evident in Fig. 1. For further geological information, please compare referred papers. For review of all in this review involved zircon analyses see Supplementary Table S3. Typical shape of zircon from different referred types of granitoids is shown in Figs. 2 and 3, relevant zircon analyses are presented in Supplementary Table S4.

Basic chemical characteristic of zircon from granitoids of different geochemical affiliation

Hafnium (Hf) is always present as a minor component of zircon forming an unlimited series of miscibility zircon–hafnon ($ZrSiO_4$–$HfSiO_4$, Correia Neves et al. 1974; Yin et al. 2013). Minerals zircon and xenotime-(Y) ((Y, HREE)PO_4) are isostructural and HREEs are relatively better suitable to enter xenotime lattice than LREEs (Mogilevsky 2007). So, minor contents of Hf, and Yb, as usually the most presented member of HREEs, can visualize the differences between zircons of different origins in a simple diagrams (Fig. 4a): zircons from all studied peralkaline rocks are, without exception, Hf- and Yb-poor. Zircons from both S- and A-type rare-metal granites may be equally strongly Hf-enriched (up to ca 0.2 apfu Hf) but zircons from A-type granites are distinctly more enriched in Yb and other HREEs; the contents of Yb in zircons from S-type rocks are often below the detection limit of EPMA. It is worth noting that in the case of A-type zircons, Hf and Yb are generally negatively correlated, and the Hf-richest A-type zircons are relatively Yb-poor. Comparing the Y and Yb contents and the resulting Y/Yb ratio (Fig. 4b), we found a distinct Y predominance with a more or less stable value of Y/Yb=18 in S-type zircons, while Y/Yb values with a large dispersion around 3.5 are typical for zircons from A-type rocks. The highest Y content of up to 0.20–0.25 apfu Y was found in zircons from peralkaline rocks (max. 11.5 wt.% Y_2O_3 in the early phase of the Khalzan Buregte pluton), while Yb reaches

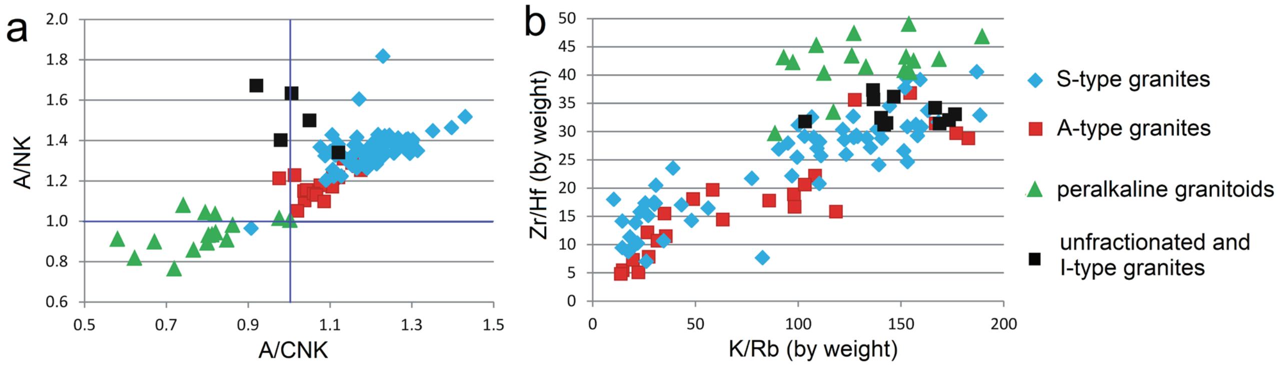
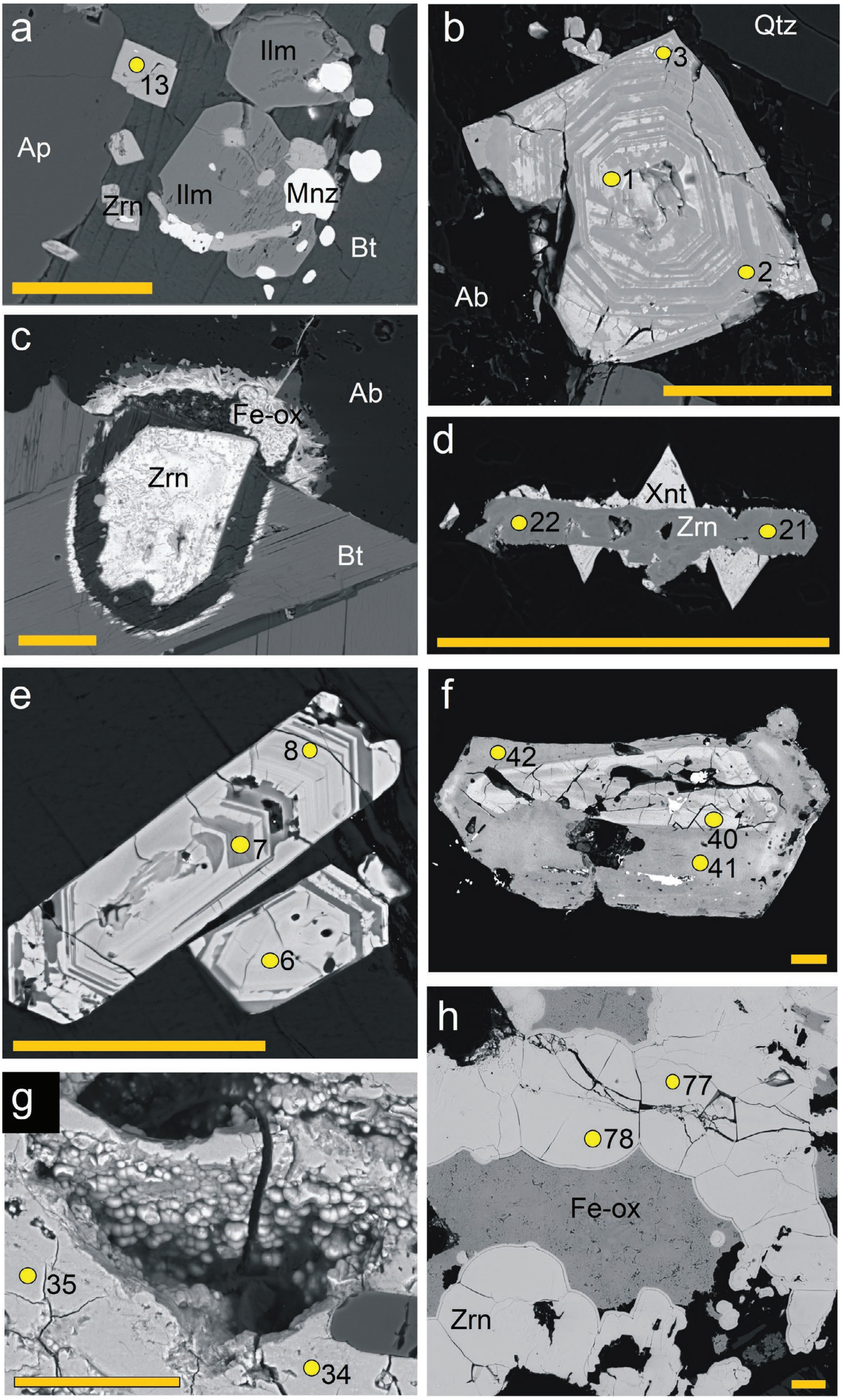


Fig. 1. Bulk-rock chemical characteristics of investigated granites: **a** — A/CNK vs. A/NK; **b** — K/Rb vs. Zr/Hf. (A/CNK=Al_2O_3/(CaO+Na_2O+K_2O), A/NK=Al_2O_3/(Na_2O+K_2O). Data sources: A-type – Eastern Krušné hory; S-type – western Krušné hory+Moldanubian pluton; I-type – Central Bohemian pluton (all author´s data); peralkaline granitoids – Europa pluton, Brazil (Costi et al. 2000) and Khalzan Buregte pluton, Mongolia (Kovalenko et al. 1995).

Fig. 2. Back-scattered electron images (BSE) of typical zircon from studied granitoids: **a** — typical association of accessory minerals in peraluminous granites: ilmenite, zircon and monazite-(Ce) embedded in biotite, Eisgarn two-mica granite, Moldanubian pluton, Griesbach, Austria; **b** — zoned zircon crystal from aplite-pegmatite dike, Megiliggar rock, Cornwall; **c** — U,Th-rich zircon in biotite surrounded by well-developed zone of radiogenic destruction of mica crystal lattice, Cínovec early biotite granite; **d** — columnar zircon crystal in association with younger xenotime-(Y), Cínovec late albite-zinnwaldite granite; **e** — well oscillatory zoned columnar zircon, Changilai biotite granite, Transbaikalia, Russia; **f** — zoned zircon, Europa peralkaline granite, Brazil; **g** — secondary zircon with cavities with papillate surface, Khalzan Buregte, syenite of the 2nd phase, Mongolia; **h** — botryoidal secondary zircon, Khan Bogd peralkaline granite, Mongolia. Scale bars 50 µm. Abbreviations of mineral names: Ab – albite, Ap – apatite, Bt – biotite, Fe-ox – Fe-oxide , Ilm – ilmenite, Mnz – monazite-(Ce), Qtz – quartz, Xnt – xenotime-(Y), Zrn – zircon. Yellow dots with numbers indicate position of zircon analyses from Supplementary Table S4.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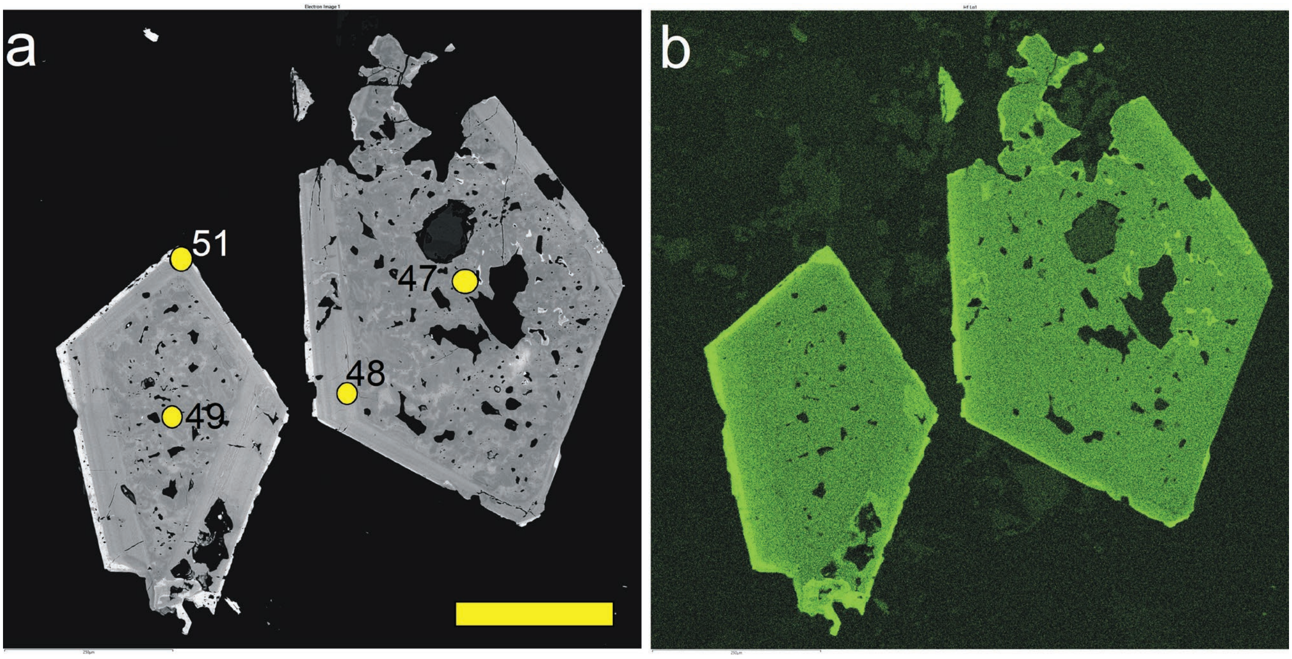

Fig. 3. Zircon from slightly peralkaline A-type Madeira albite granite, Brazil, with distinct Hf-enriched rims: **a** — BSE image; **b** — distribution of Hf. Scale bar 200 μm. Yellow dots with numbers indicate position of zircon analyses from Supplementary Table S4.

the highest contents of 0.06 apfu (ca. 5 wt.% Yb_2O_3) in zircons from A-type biotite granite from Cínovec.

Among radioactive elements, U predominates in zircons from S-type rocks, while Th predominates in zircons from A-type rocks; zircons from peralkaline rocks are both U- and Th-poor (Fig. 4c). During fractionation, with decreasing Zr/Hf values, both U and Th tend to slightly increase (Fig. 4d).

Scandium (Sc) is a common minor component in zircon, although rarely present in more than trace amounts: contents exceeding 0.04 apfu in either S- or A-type zircon are rare, with the maximum of ca. 0.1 apfu Sc (3.36 wt.% Sc_2O_3). Sc contents in zircons from peralkaline rocks usually do not exceed the detection limit of EPMA (Fig. 4e).

Zircons from fractionated facies of S- and A-type granites often contain 0.2–0.3 apfu F (ca. 1.75–2.5 wt.% F), while zircons from peralkaline rocks only scarcely reach more than 0.05 apfu F (Fig. 4f).

Due to the isostructural crystal lattice of zircon and xenotime, the coupled substitution $ZrSiO_4$ vs. (Y,HREE)PO_4 is expected to be the dominant mechanism of REE binding in zircon. However, Fig. 4g shows a more complex REE behavior. Although we did not analyze all REEs, the analyzed selection (Y, Dy, Er, Yb) certainly represents more than 95 % of the total REE+Y contents (Nardi et al. 2013), and its comparison with the P contents is correct. In S-type zircons, P(apfu)>>Y+REE(apfu), and a substantial part of P is balanced via 2Si↔P+Al substitution, similarly as in the case of other silica minerals crystallized from strongly peraluminous P-rich melt (alkali feldspars (London 1992), garnet (Breiter et al. 2005c), or topaz (Breiter & Kronz 2004)), and/or additionally with the entry of Fe and Ca to the Zr position. In contrast, many zircons from A-type rocks and all zircons from peralkaline rocks have REE(apfu)>>P(apfu), which is, at minimum contents of M^{5+} and M^{6+} cations, difficult to explain; perhaps ZrO↔REE(OH,F) substitution may play a role.

Evaluating Fig. 4 as a whole, the combination of the Y, Yb, (Y+REE) and P contents is able to indicate the pertinence of a particular zircon grain to one of the three basic geochemical rock types with a satisfactory probability.

Evolution of zircon chemistry during fractionation of typical plutons

Here, differences in evolutionary trends of zircon from typical plutons of different geochemical/geotectonic affiliation will be shown.

First, we will check the analytical totals of EPMA. If the analytical protocol includes all elements present in quantities higher than the relevant analytical limits, the analytical sum should ideally equal 100 wt.%. If the detected sum differs from 100 wt.% by more than the expected analytical error, the low sum is usually explained as a result of crystal lattice destruction due to radioactive irradiation (Nasdala et al. 2009); the reduction in the analytical sum should therefore be roughly proportional to the contents of radioactive elements. Figure 5a, c, e, g shows this relation on the example of typical plutons of different geochemical types, and we can generally see a good negative correlation between (U+Th) contents and analytical sums in all cases. But at the same time, a number of samples

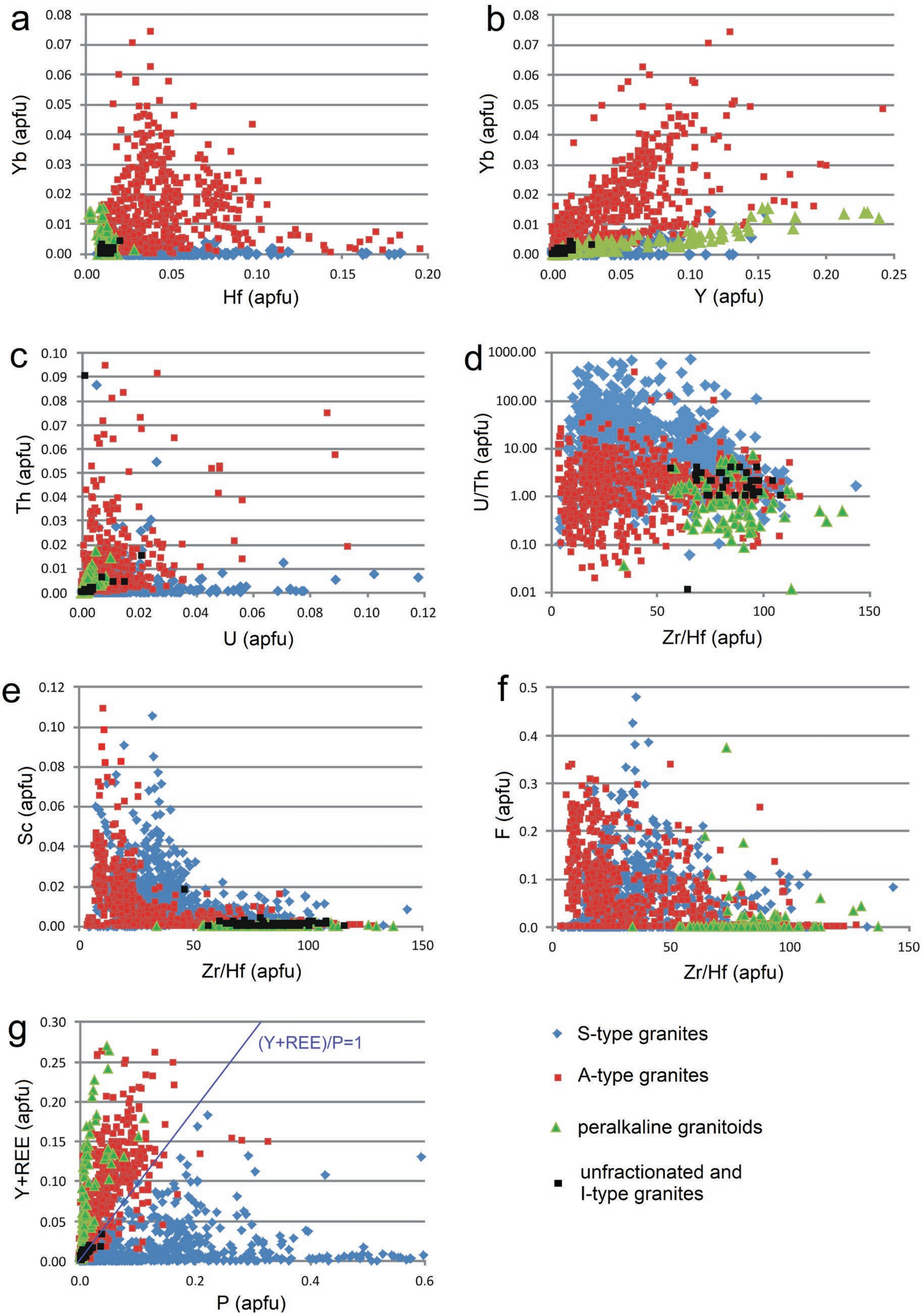

Fig. 4. Chemical composition of zircon from granitoids of different geochemical affiliation: **a** — Hf vs. Yb; **b** — Y vs. Yb; **c** — U vs. Th; **d** — Zr/Hf vs. U/Th; **e** — Zr/Hf vs. Sc; **f** — Zr/Hf vs. F; **g** — P vs. Y+REE. Content of F in zircon from unfractionated and I-type granites is almost always below detection limit of EPMA.

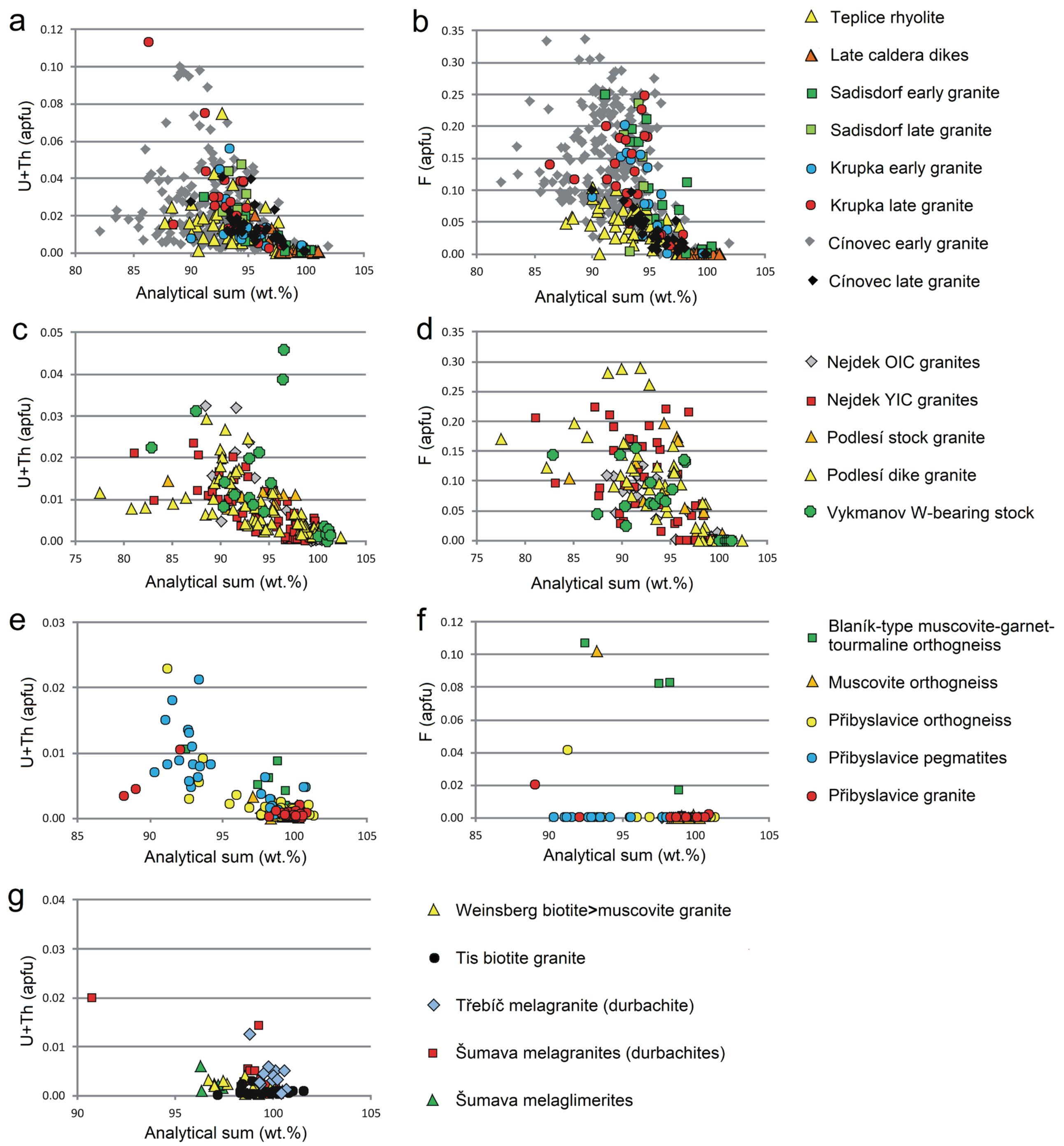

Fig. 5. Correlation between analytical total and chemical composition of zircon from selected investigated plutons: **a, c, e, g** — analytical sum vs. U+Th; **b, d, f** — analytical sum vs. F. Zircon from primitive granitoids is F-poor (below detection limit of EPMA); a, b — Teplice caldera and associate granites; c, d — Nejdek pluton; e, f — Moldanubian orthogneiss and associate rocks; g — unfractionated graitoids.

with low to very low analytical sums can be found in all plutons, even though they have low U+Th contents, i.e., a strong irradiation is not probable. An explanation of this phenomenon remains speculative.

The following Figure 5b, d, f shows a significant negative correlation between the analytical sums and F contents: this may indicate that the zircon structure in a F-rich (and H_2O-rich) environment was influenced by the entry of F^- and probably also OH^- into the oxygen positions following the substitution $(SiO_4)^{4-}\leftrightarrow 4(OH)^-$, or $(SiO_4)^{4-}\leftrightarrow 4F^-$. This explanation is supported by the frequent Si–Zr imbalance and distinctly lower occupancy of the Si-site than the Zr-site in the low-total zircons.

As shown by Fig. 5, more than one half of analyzed zircon grains from RMGs have analytical sums of <95 wt. %. However, this may be a serious analytical problem for LA-ICP-MS analyses when many authors make their work easier by normalizing the analytical results to a sum of presumed 100 wt. % instead of using an internal standard.

As mentioned earlier, zircon ($ZrSiO_4$) and hafnon ($HfSiO_4$) are miscible without limitations, and the increase in Hf content, i.e., a decrease in the Zr/Hf value, is one of the most reliable indicators of magmatic fractionation. The gradual increase in Hf content, i.e. the decrease in Zr/Hf value, is often visible even within individual crystal; Hf-enriched rims are clearly visible in BSE (Fig. 3a). In this case, the Hf content in rim reaches up to 14 wt. % HfO_2.

Diagrams Zr vs. Hf (Fig. 6) show not only the absolute contents of both elements and their ratio but also the sum of Zr+Hf which should be ideally 1 apfu. The smaller is the actually determined Zr+Hf sum, the higher is the content of other elements, impurities, in a particular zircon grain. In the case of the Orlovka, Cínovec, Nejdek and Khalzan Buregte plutons, Zr+Hf contents are reduced to 0.6–0.8 apfu, i.e., the sum of other elements, mainly Y, REE, U, Th, Sc but also Al, Ca and Fe may reach up to 0.2–0.4 apfu.

The Y/Yb value was generally examined already in Fig. 4. It can be, however, examined specifically for individual plutons (Fig. 7). Zircon from many plutons keeps the Y/Yb value nearly constant during the whole magmatic evolution. This is typical for less fractionated granitic systems (Central Bohemian, Moldanubian and Třebíč plutons) (Fig. 7a–c), among RMGs for the Cornubian batholith (Fig. 7d). Zircons from the Nejdek pluton (Fig. 7e) show a wide Y/Yb dispersion but generally also keep a single array. However, in some plutons, zircons belonging to two clearly different trends were found. For example in Altenberg–Teplice caldera, zircons from rhyolite and the oldest Preiselberg granite have Y/Yb values around 10, while the Y/Yb value around 2 was found in the late Krupka and Sadisdorf zircons; zircons from the Cínovec cupola vary between Y/Yb=2–5 (Fig. 7f). At Khalzan Buregte, the early peralkaline phases contain Y-enriched zircon (Y/Yb=15), while zircons from the latest subaluminous RMGs are relatively Yb-enriched (Y/Yb=3, Fig. 7g). At Orlovka, the Y/Yb value decreased from the early biotite granites (Y/Yb=12) to late lepidolite and layered zinnwaldite granites (Y/Yb=1.6) which is the lowest value found among all studied plutons (Fig. 7h). A similar shift to lower values during pluton evolution was found also at Madeira, Brazil (Breiter et al. 2025).

Scandium only rarely forms its own minerals, but zircon, along with columbite, is one of minerals relatively often hosting notable minor amounts of Sc (Hreus et al. 2021). The contents of Sc in zircon usually distinctly increase with magma fractionation, i.e., with a decreasing Zr/Hf value (Fig. 8). Granites from the eastern Erzgebirge are generally enriched in Sc (Hreus et al. 2021), and zircons from late granite facies from this area are the Sc-richest among all analyzed in this paper: up to 0.08 apfu at Cínovec and 0.11 apfu at Sadisdorf (Fig. 8a). Values up to ca. 0.05 apfu were found in other fractionated RMGs (Cornwall, Nejdek pluton and some of the Přibyslavice rocks; Fig. 8b–d), while contents lower than 0.01 apfu are typical for other studied RMGs (Orlovka, Beauvoir), all peralkaline rocks and all less evolved granitoids (Fig. 8e–h).

Uranium behaves generally incompatible in minerals crystallizing from granitic melt, zircon including. Accordingly, U contents in zircons in most plutons increase during the fractionation, reaching max. ca 0.1 apfu at Cínovec but usually being <0.04 apfu (Fig. 9a–c). An exception is the Beauvoir pluton with a significant decrease in U at the transition to the most fractionated B1 facies (Fig. 9d). Bulk-rock content of thorium usually decreases during fractionation of peraluminous melt, while increases during fractionation of the A-type melt. Accordingly, Th contents in zircon from A-type granites increase with the fractionation process (Cínovec, Orlovka; Fig. 9e, f), while low Th contents and no distinct trend were found in zircons from the Nejdek pluton (Fig. 9g) and other S-type systems (Cornwall, Central Moldanubian pluton, Moldanubian orthogneiss). Zircons from evolved leucogranites at Beauvoir are Th-free (below the detection limit of EPMA), and zircons from Madeira pluton, although from A-type granites rich in thorite, are also Th-poor (<0.05 apfu). At Khalzan Buregte, zircons from peralkaline rocks are Th-free, while zircons from the latest subaluminous phase are strongly Th-enriched, which is typical for A-type rocks (Fig. 9h).

Extremely high contents of some minor elements

Besides the aforementioned major (Si, Zr, Hf) and common minor (Th, U, Y, REE) elements, two more groups of elements can constitute a notable part of the chemical composition of zircon. The first group is represented by heavy metals with other than 4^+ charge – W, Nb, Ta, Bi, Sc, and Pb. Contents up to 2 wt. % WO_3 were found in the Amazonian A-type granites and in the Podlesí and Krásno S-type granites from the Nejdek pluton, and contents up to 2.5 wt. % WO_3 were found in A-type granite of the Kimi stock, Finland. High Nb contents were locally found in zircon from all investigated granite plutons: max. 0.5 wt. % Nb_2O_5 at Khan Bogd (Mongolia), max. 1.5 wt. % Nb_2O_5 at Kimi and Cínovec, and max. 2 wt. % Nb_2O_5 at Podlesí in the Nejdek pluton. (Even higher contents of max. 6.6 wt. % Nb_2O_5 were found by Smith et al. (1991) in zircon from the Thor Lake alkali syenite.) The highest Ta contents, up to 0.5 wt. % Ta_2O_5, were found at Cínovec. Zircon substantially enriched in Bi and Sc is specific for both granite types in the Erzgebirge: max. 3 wt. % Bi_2O_3 at Krupka and Cínovec, max. 7 wt. % Bi_2O_3 at Hora Svaté Kateřiny (all A-type granites) and max. 7 wt. % Bi_2O_3 in S-granite at Podlesí. The highest scandium contents in zircon of max. 3.5 wt. % Sc_2O_3 were found in the Sadisdorf A-granite and max. 2 wt. % Sc_2O_3 at Podlesí. Erratic values up to 2 wt. % PbO were found in zircon from the Teplice rhyolite, eastern Erzgebirge. The interpretation of the mode of entry of these elements into the zircon structure would be rather speculative. Nevertheless,

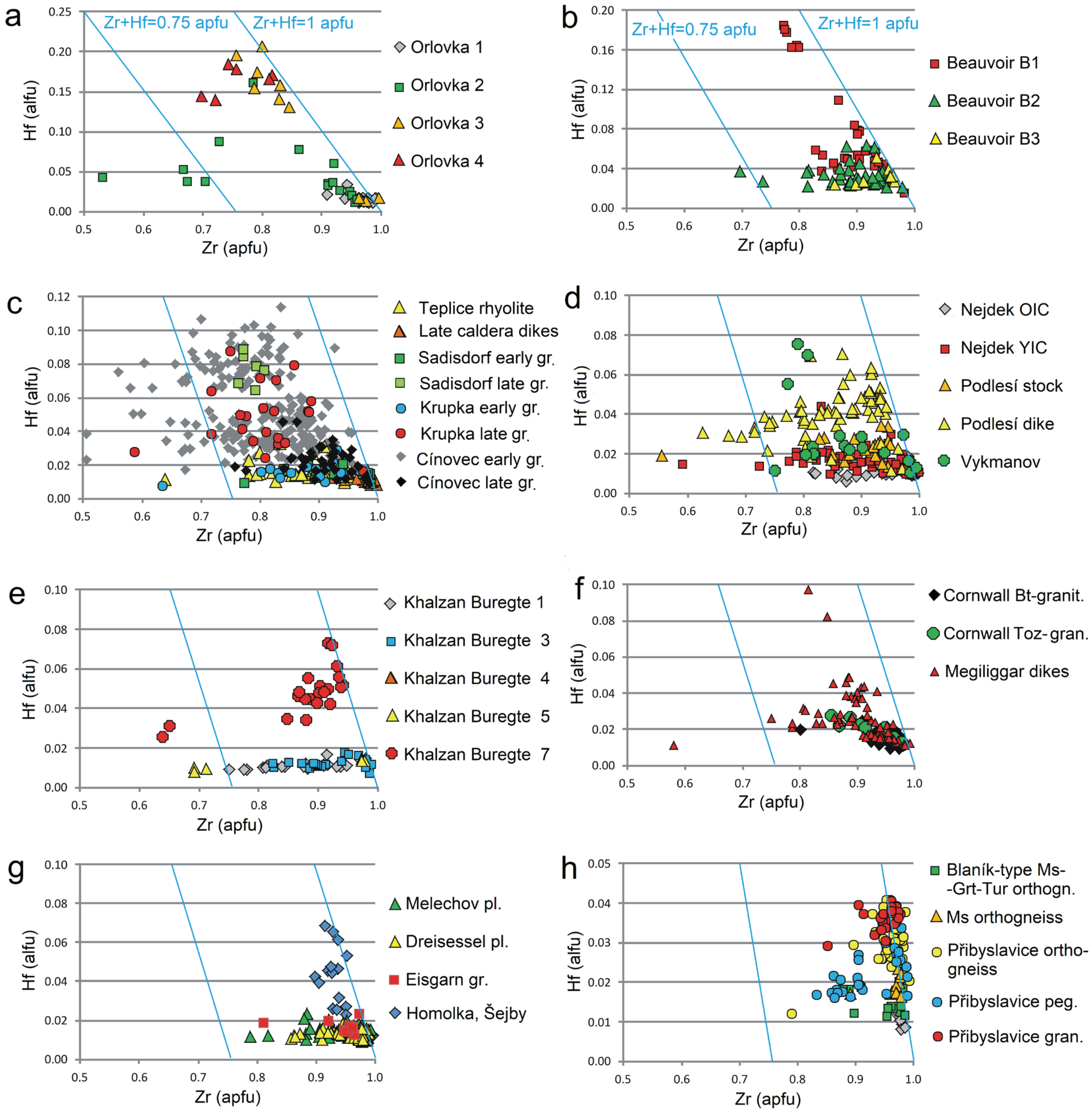

Fig. 6. Contents of Zr and Hf in zircon from typical plutons: **a** — Orlovka; **b** — Beauvour; **c** — Teplice caldera and associated granites; **d** — Nejdek pluton; **e** — Khalzan Buregte; **f** — Cornwall; **g** — Moldanubian pluton; **h** — Moldanubian orthogneiss and associated rocks. Blue lines show sum of Zr+Hf=1 and Zr+Hf=0.75 apfu, i.e. expected contents of other elements in the Zr-site equals 0 and 0.25 apfu, respectively.

post-magmatic hydrothermal processes are probably responsible for the high concentrations of Bi and Pb, whereas zircon grains enriched in W, Nb and Sc are more likely magmatic. On the other hand, high concentrations of Al (up to 5 wt.% Al_2O_3), Ca (up to 4 wt.% CaO) and Fe (up to 5 wt.% FeO, all in the S-type granites), and to a lesser extent also Mn and Mg, are a result of low-temperature diffusion in the damaged structure of zircon (compare Breiter et al. 2025).

Discussion

Zr/Hf and Y/Yb values as a discriminator of zircons of different provenance?

Already 25 years ago, Pupin (2000) proposed to use Hf and Y contents in zircon as simple indicators of the geotectonic provenance of the parent magma. Later, Belousova et al.

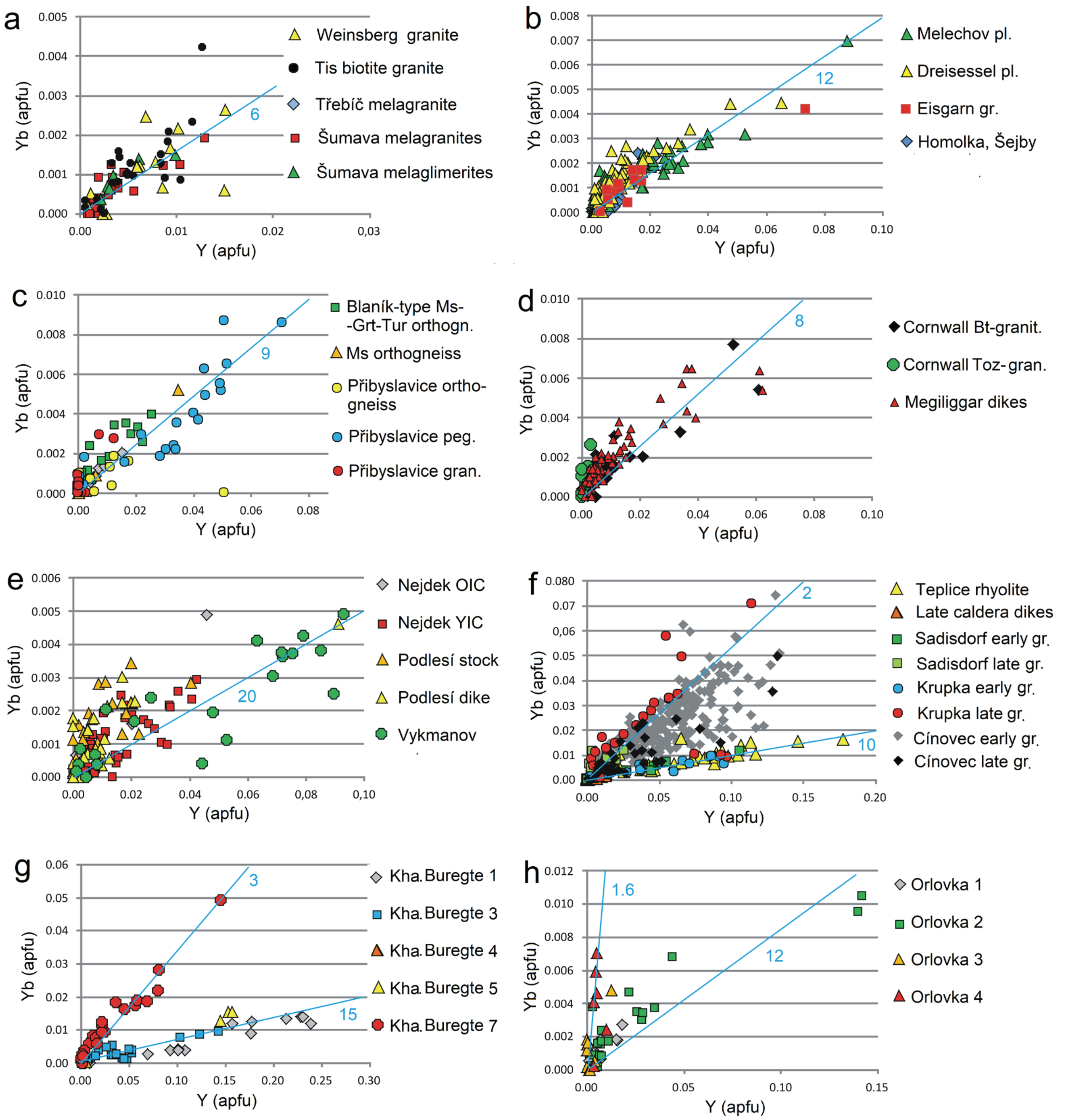

Fig. 7. Contents of Y and Yb in zircon from typical plutons: **a** — unfractionated granites; **b** — Moldanubian pluton; **c** — Moldanubian orthogneiss and associated rocks; **d** — Cornwall; **e** — Nejdek pluton; **f** — Teplice caldera and associated granites; **g** — Khalzan Buregte; **h** — Orlovka. Blue lines show Y–Yb correlation lines, blue numbers the Y/Yb values (Upper-crust atomic Y/Yb value is 19.5, Rudnick & Gao 2003).

(2002) and Grimes et al. (2015) proposed a more complicated set of discriminating parameters including, in addition to Hf and Y, also Ti, Nb, Ce, Yb, U, Th etc. The success rate of a correct classification of each sample seemed good but the practical application was far too complicated. General diagrams in Fig. 4a, b, g look promising. Nevertheless, the real possibilities of a successful use of the Pupin's diagram or a similar simple diagram should be tested in terms of a statistically significant set of zircon data.

With respect to the notoriously low analytical totals for zircon from strongly evolved rocks, priority should be given to the use of Zr/Hf values over Hf contents themselves. The Zr/Hf values are 33–38 (by weight) in chondrites (Anders & Grevesse 1989; Barrat et al. 2012) and 35.6 by weigh or ca 70 by atoms in the Earth crust (Rudnick & Gao 2003) but these values vary considerably in zircons. Pupin (2000) found Zr/Hf values of ca 130 (by atoms) in zircon from mantle-derived plagiogranites and alkaline syenites, while majority of

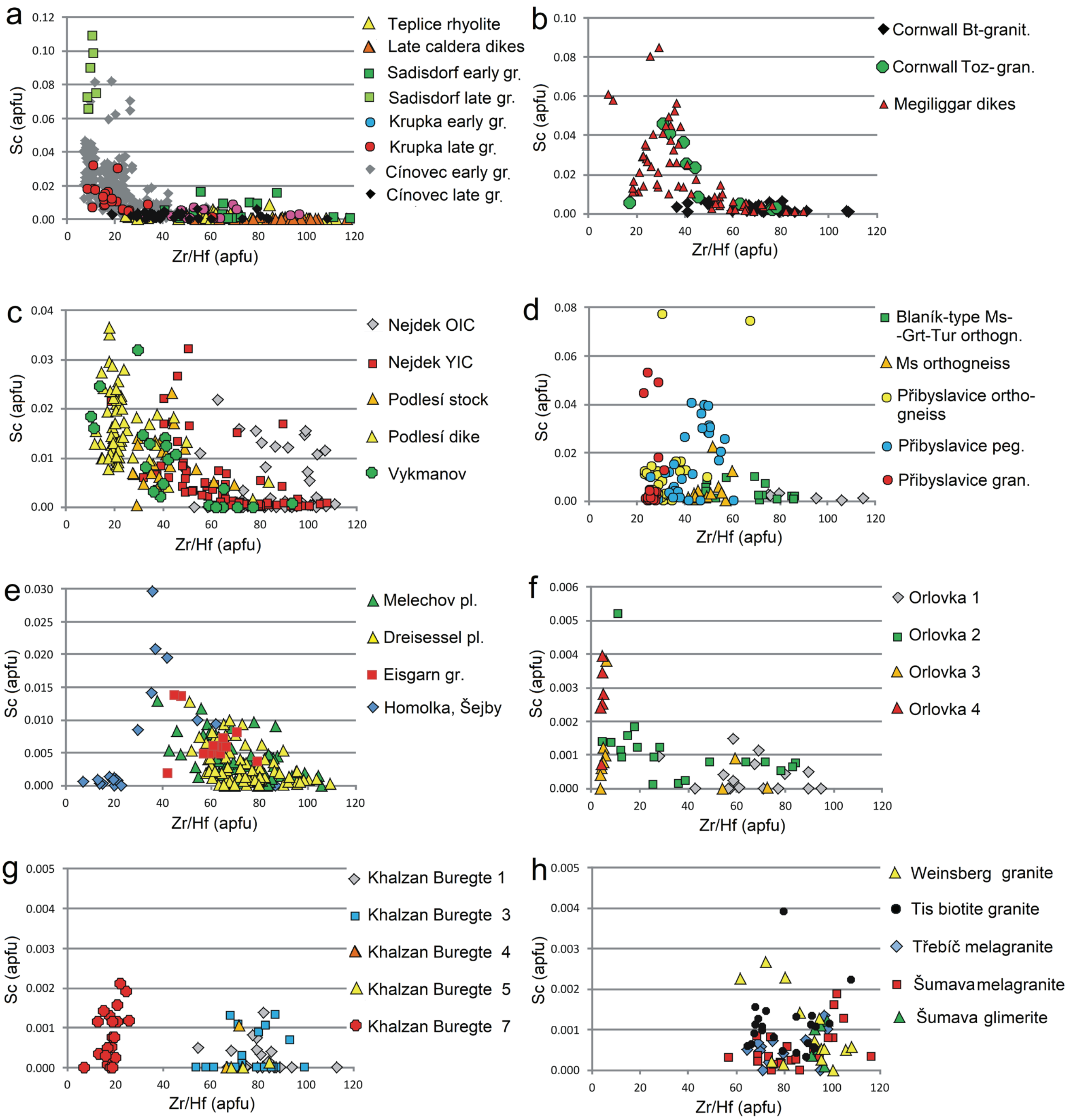

Fig. 8. Chemical composition of zircon from typical plutons in terms Zr/Hf vs. Sc: **a** — Teplice caldera and associated granites; **b** — Cornwall; **c** — Nejdek pluton; **d** — Moldanubian orthogneiss and associated rocks; **e** — Moldanubian pluton; **f** — Orlovka; **g** — Khalzan Buregte; **h** — unfractionated granites.

crustal-derived rocks contain zircon with atomic Zr/Hf values of 70–90. Due to the distinct difference between Zr and Hf distribution coefficients in zircon (Linen & Keppler 2002), the Zr/Hf value decreases with progressive fractionation of both S- and A-type melts, and distinctly lower values down to 10–20 are typical for rare-metal granites and pegmatites (e.g., Černý et al. 1985). In peralkaline complexes, Zr/Hf fractionation is negligible (Linen & Keppler 2002). Taken together, the Zr/Hf values may serve as a sensitive indicator of the general fractionation evolution of silicate melts (Fig. 10a).

Pupin (2000) supposed Y to be a robust indicator of geochemical/geotectonic affiliation of zircon from peraluminous leucogranites and calc-alkaline granitoids (mostly <0.2 wt.% Y_2O_3) through alkaline rocks (0.2–1 wt.% Y_2O_3) to tholeiitic plagiogranites (mostly 0.5–2.5 wt.% Y_2O_3). Looking at Fig. 4b, it is clear that in our dataset the three basic granitoid types

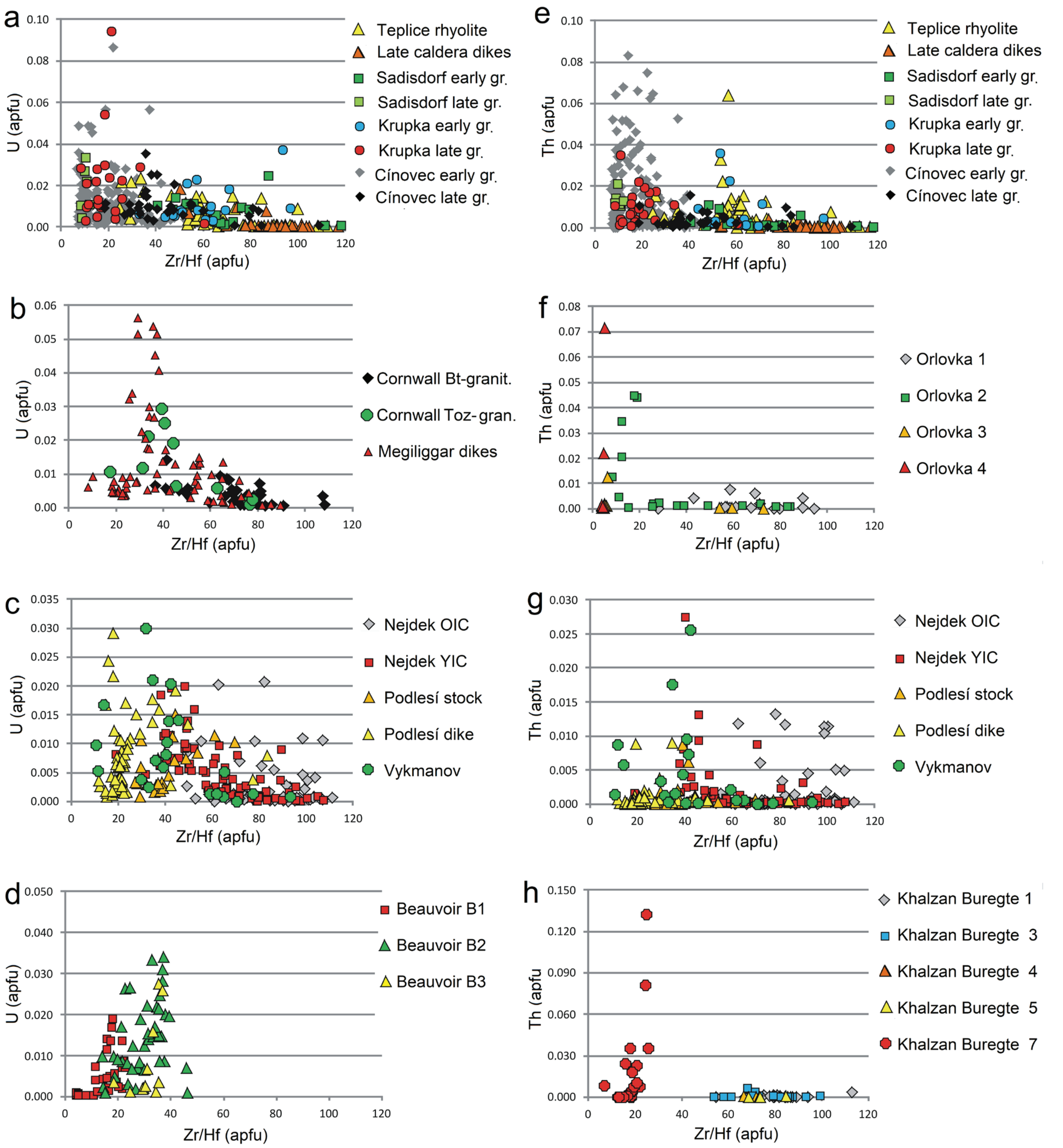

Fig. 9. Chemical composition of zircon from typical plutons in terms: **a–d** — Zr/Hf vs. U; **e–h** — Zr/Hf vs. Th; a — Teplice caldera and associated granites; b — Cornwall; c — Nejdek pluton; d — Beauvoir; e — Teplice caldera and associated granites; f — Orlovka; g — Nejdek pluton; h — Khalzan Buregte.

completely overlap in their Y contents; the Yb contents and especially the Y/Yb values look more promising.

Bulk crustal Y/Yb values are ca. 10 by weight or 19.5 by atoms (Rudnick & Gao 2003). Multiple field evidence confirms the dependence of bulk-rock Y/Yb fractionation on melt peraluminosity: this value mostly increases during the fractionation of strongly peraluminous S-suites but systematically decreases during the fractionation of A-suites; during the crystallization of peralkaline plutons, bulk-rock Y/Yb values, similarly like Zr/Hf values, remain stable (Fig. 10a).

However, a more complicated evolution was found for mineral zircon itself. Experimentally proposed distribution coefficients of Y and Yb in zircon varied in broad intervals (Thomas et al. 2002; Rubato & Hermann 2007; Nardi et al. 2013), being nearly the same for the two elements (Thomas et al. 2002), or the coefficient for Yb was 2–3 times higher (other

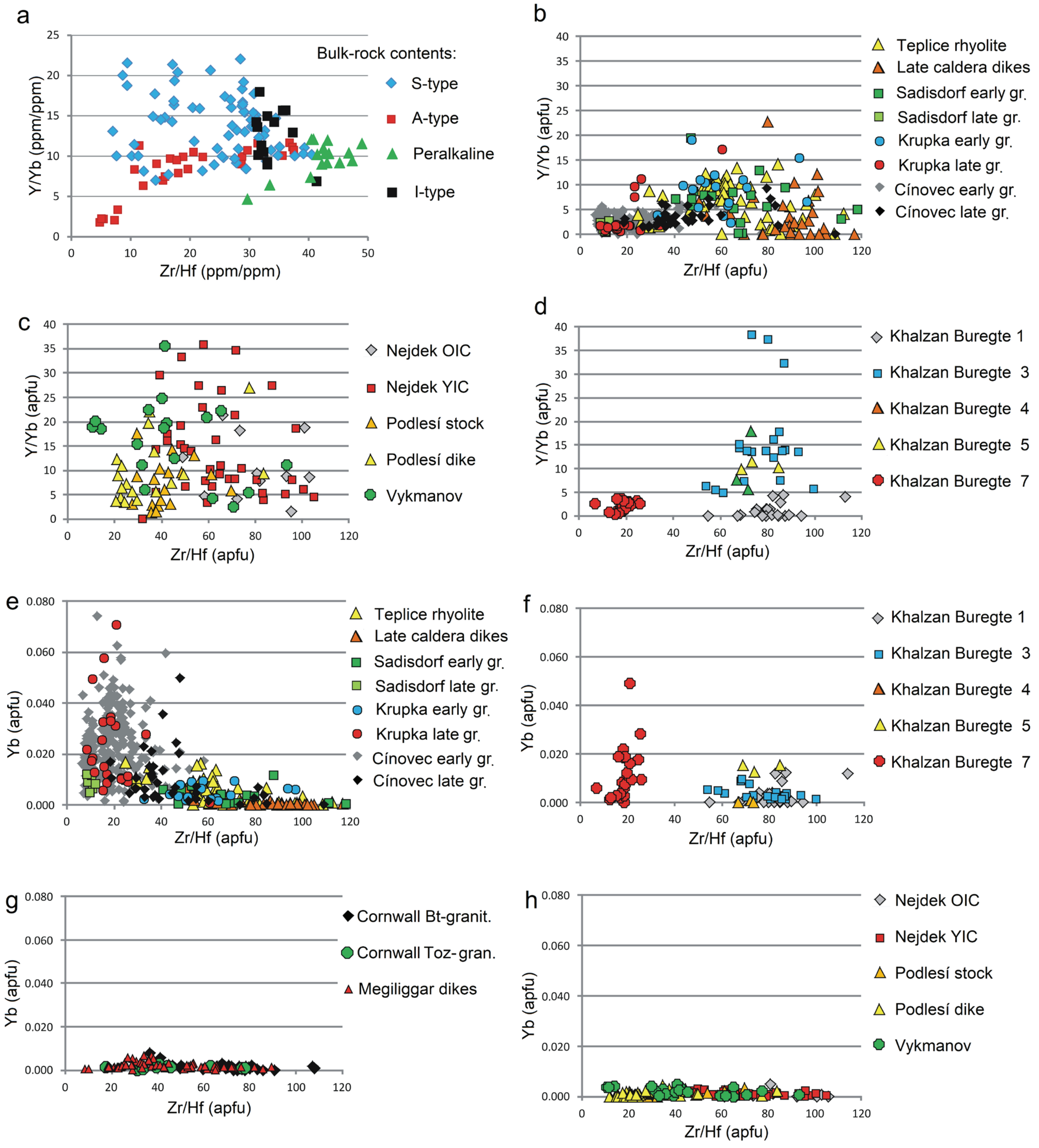

Fig. 10. Relation between Zr/Hf, Y/Yb and Yb values in bulk rocks and in zircon: **a** — Zr/Hf vs. Y/Yb in bulk rock; **b–d** — Zr/Hf vs. Y/Yb in zircon from typical plutons; **e–h** — Zr/Hf vs. Yb in zircon from typical plutons: b — Teplice caldera and associated granites; c — Nejdek pluton; d — Khalzan Buregte; e — Teplice caldera and associated granites; f — Khalzan Buregte; g — Cornwall; h — Nejdek pluton. Bulk-rock data for Fig. 10a as in Fig. 1.

experiments). It appears from the experiments, and this is confirmed by natural evidence, that the evolution of the Y/Yb values in zircon depends on the composition of the fractionated magma (P, F, water content) rather than on the original Y and Yb contents in the initial melt.

If large sets of analyses of zircon grains of various provenances are used (Fig. 10b–d), decreasing averages or median values are seen in a succession from paraluminous to subaluminous to peralkaline rocks, but a large overlap of values of individual analyses is observed at the same time. The Zr/Hf vs.

Yb diagram (Fig. 10e–h) seems to be somewhat more promising: zircons with high Yb at low Zr/Hf certainly belong to the A-suite, and zircons slightly enriched in Yb at high Zr/Hf will be probably of peralkaline affiliation. Zircons with low Yb, unfortunately, may belong to either of the principal granitic suites.

The (Y+REE)/P values in zircon are sensitive to melt peraluminosity. They are mostly <1 in peraluminous S-type melt and even decrease to 0.01 during its fractionation and further increase in peraluminosity (Fig. 11a). Zircons from subaluminous A-type granites have (Y+REE)/P values >1 (mostly 1–8, Fig. 11b), and zircons from peralkaline granites have always values >1 (mostly 1–10, Fig. 11c). But even in this case, some plutons deviate from the general geochemical trend: the strongly peraluminous Vykmanov intrusion (western Erzgebirge) contains zircon grains with systematically (Y+REE)/P values >1 (Fig. 11a), while the A-type Sadisdorf cupola contains zircon grains with (Y+REE)/P values <1 (Fig. 11b).

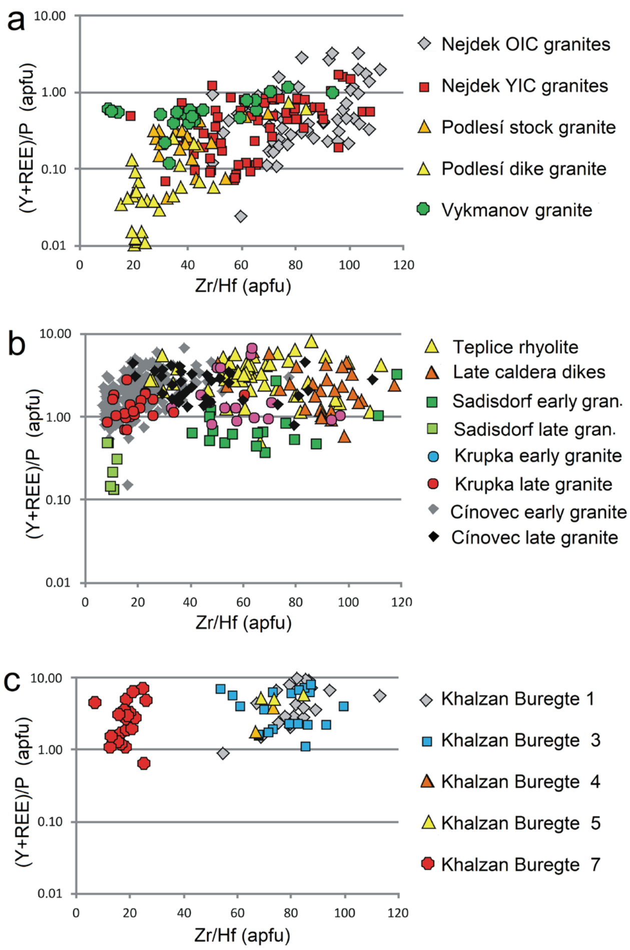

Fig. 11. Relation between Zr/Hf vs. (Y+REE)/P in zircon from typical plutons indicates some principal differences in chemical evolution of zircon from different geochemical types of granitoids: **a** — Nejdek pluton; **b** — Teplice caldera and associated granites; **c** — Khalzan Buregte pluton.

The conclusion of our investigation is therefore not very optimistic: the chemical composition of zircon is mostly only indicative of its source. It provides information about the composition of parental melt and the conditions of its crystallization but an unambiguous assignment of the analyzed grain to the source melt type is often questionable.

Conclusions

Despite the ambiguous results of the previous discussion, it is possible to list the characteristic features of zircons from the four main granitoid types:

Peralkaline rocks: In peralkaline granitoids containing primary zirconosilicates, represented by the Khan Bogd and Khalzan Buregte plutons (Mongolia), most zircon grains are secondary, originating from primary Zr silicates in the hydrothermal stage. They often form globular or radial aggregates. The Zr/Hf value is >50. Chemical compositions typically show high contents of Y, moderate contents of REE (thus high Y/Yb values) together with high (Y+REE)/P values, low contents of U, Th and Sc, and low analytical totals. In peralkaline rocks containing zircons as the only primary Zr mineral (Europa pluton, Brazil), zircon grains are late, euhedral and poor in all minor elements.

Evolved A-type rocks: The exclusive primary Zr mineral is zircon, often a relatively late mineral, mostly of orthomagmatic origin. Typical features include the extreme dispersion of Zr/Hf values (120→5), enrichment in HREE resulting in low Y/Yb values and high (Y+REE)/P values. Zircon is often enriched in Sc, locally also in Nb or Bi. Low analytical sums are common.

Evolved S-type granites: Relatively early crystallizing euhedral zircon is the only host of Zr. The dispersion of Zr/Hf values is wide (110→10), zircon is often rich in P and Al, the (Y+REE)/P value usually <<1. Zircon from late granite facies near the magmatic/hydrothermal transition yield low analytical sums and often is enriched in W, Nb and Bi.

Primitive S-type and I-type granitoids: Early crystallizing euhedral zircon is poor in all trace elements.

Generally, zircon is chemically variable at all scales of research. Detailed studies show that the contents of minor elements varied within the same crystal/thin section/sample/rock facies much more than usually expected from individual analyses. The effect of the geotectonic environment of formation is particularly evident in late strongly fractionated rocks, while zircons from less evolved rocks of all geochemical types are similar.

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