GEOLOGICA CARPATHICA, APRIL 2006, 57, 2, 131–142

Saturnin, R language script for application of accessory-mineral saturation models in igneous geochemistry

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(Manuscript received January 11, 2005; accepted in revised form June 16, 2005)

Abstract: Accessory minerals play a crucial role in the petrogenesis of granitic rocks. They control the response of isotopic systems (U–Pb, Lu–Hf, Sm–Nd) and rule the geochemical variation of many important trace and minor elements during partial melting and fractional crystallization. The experimental effort in the past thirty years has resulted in the formulation of saturation models with manifold applications in igneous geochemistry. Numerical simulations show that the zircon saturation thermometer is rather insensitive to analytical errors, the presence of a minor inherited component, as well as moderate accumulation of feldspars and some ferromagnesian minerals (Ca-poor pyroxenes, less so olivine). However addition of even minor cumulus Ca-pyroxene or Ca-amphibole would quickly render the calculated temperatures too low. Apatite saturation thermometry is a poor tool for felsic metaluminous rocks, being oversensitive to errors in the phosphorus determination as well as the presence of extraneous apatite. Even stronger element of uncertainty is added for peraluminous lithologies, when the increased apatite solubility is inadequately accounted for by the current models and where other phosphorus-bearing minerals, most importantly feldspars and monazite, come into play. The newly developed software *Saturnin* (*http://www.gla.ac.uk/gcdkit/saturnin*) written in the freeware R language performs otherwise tedious calculations of zircon, monazite and apatite saturation in igneous rocks. While the Windows users would probably find it easier to access the programme as a part of the larger package *GCDkit* (*http://www.gla.ac.uk/gcdkit*), on Macintosh and Linux it can be used as a stand-alone application.

Key words: software, igneous geochemistry, fractional crystallization, partial melting, geothermometry, zircon, apatite, monazite.

Introduction

Recent studies confirm the crucial role played by accessory minerals in the petrogenesis of granitoid rocks. These minerals, for the most part, control the response of isotopic systems (U–Pb, Lu–Hf, Sm–Nd) and rule the geochemical variation of many important trace and minor elements (e.g. Zr, P, REE, U, Th) during partial melting and subsequent fractionation of the magma (Gromet & Silver 1983; Miller & Mittlefehldt 1984; Sawka 1988; Watt & Harley 1993; Bea 1996; Ayres & Harris 1997; Hoskin et al. 2000).

In particular three minerals, vital in geochronology and isotopic geochemistry, have been the subject of copious studies of natural and experimental systems: zircon (Watson & Harrison 1983; Harrison & Watson 1983; Watson 1996; Baker et al. 2002; Miller et al. 2003; Hanchar & Watson 2003; Cherniak & Watson 2003), apatite (Watson & Capobianco 1981; Harrison & Watson 1984; London 1992; Bea et al. 1992; Pichavant et al. 1992; Wolf & London 1994, 1995; Cherniak 2000) and monazite (Rapp & Watson 1986; Montel 1993; Wolf & London 1995; Cherniak et al. 2004).

The experimental effort of these as well as numerous other authors resulted in formulation of saturation models with manifold applications in igneous geochemistry. The current paper provides a critical overview of those for zircon, apatite and monazite, a summary of the relevant formulae and their practical implementation in the freeware R language.

Applications of saturation models in igneous geochemistry

Fractional crystallization

As the fractionation of accessory minerals has profound effects on the trace-element budget of the parental magma, a good understanding of the factors controlling their crystallization is a fundamental issue in igneous petrogenesis (Evans & Hanson 1993; Bea 1996; Hoskin et al. 2000). The growth of phases like zircon, apatite or monazite seems to be governed by geochemical species concentrated in the accessory but incompatible in the main rock-forming minerals. These elements, termed essential structural constituents (ESC) by Hanson & Langmuir (1978), are Zr in zircon, P in apatite, P and LREE (Ce) in monazite. At the onset of magma crystallization, such a trace element would behave incompatibly, gradually increasing its concentration in the magma until a required saturation threshold is reached (point *S* in Fig. 1a). For this segment of the crystallization path *(OM–S)*, the proportion of the remaining melt in each magma batch has to be reduced significantly by crystallization of the major rock-

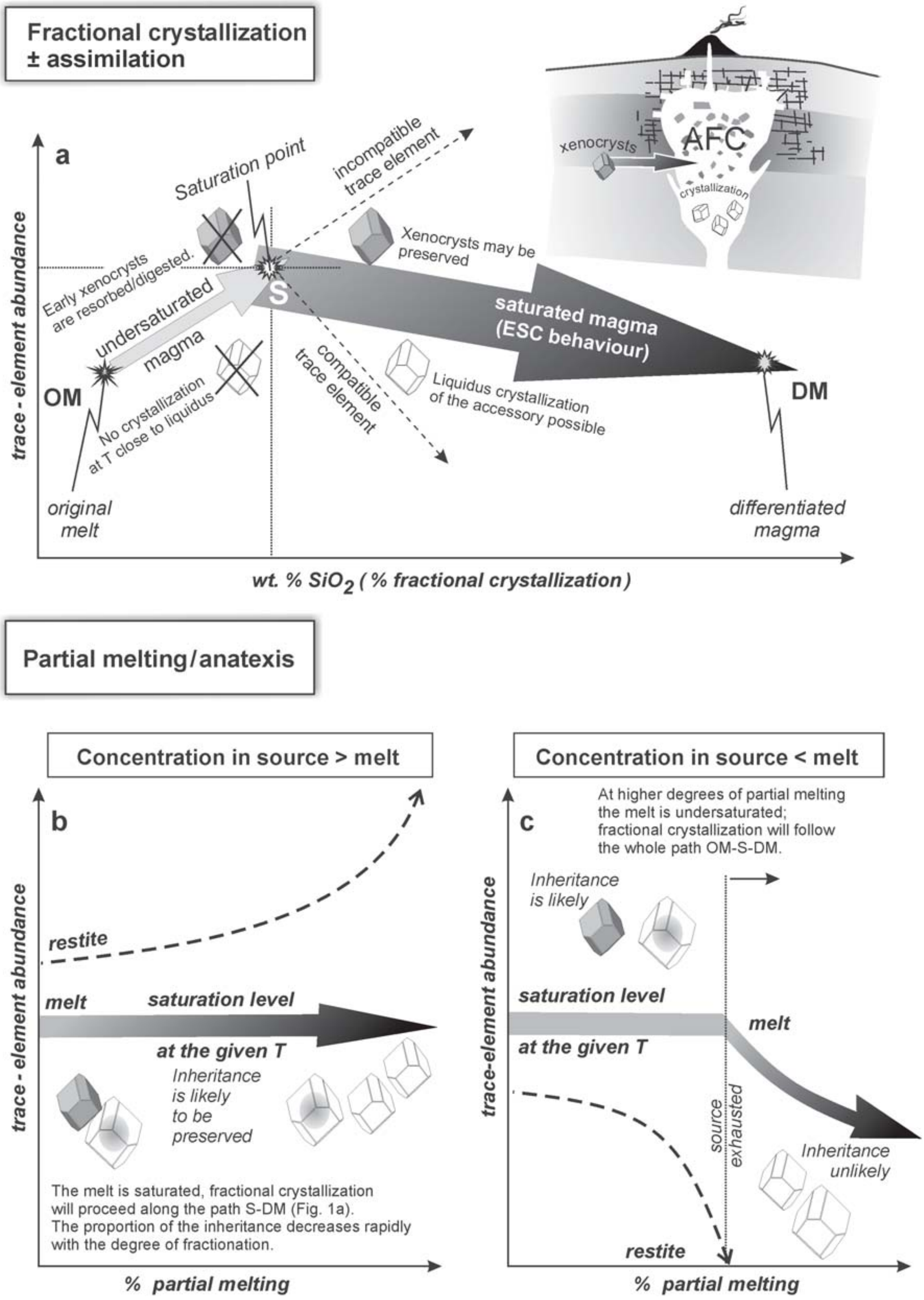


Fig. 1. a — Temporal development of trace-element abundance in a hypothetical magmatic suite evolving by fractional crystallization. The behaviour of the trace element swaps from incompatible (OM–S) to that of an essential structural constituent (ESC: S–DM). The liquidus crystallization of the corresponding accessory mineral is possible only after the saturation level has been reached, i.e. at or beyond the point S. In part after Evans & Hanson (1993); see text for discussion. **b–c** — Trace-element contents in a partial melt and a restite as a function of melting degree. In the first case (b) the concentration of the ESC in the source is higher and in the second (c) lower than the saturation level (= concentration in the melt). After Watson & Harrison (1984).

forming minerals for the magma to become saturated. As a consequence, the growth of the accessory crystals is possible only at a temperature significantly below the liquidus.

The crystallization of the accessory phase at temperatures close to liquidus may commence at the point *S*, when the element starts acting as an essential structural constituent. Its concentration is from this point on buffered by the accessory growth at a saturation level (Hanson & Langmuir 1978; Evans & Hanson 1993). However this level is unlikely to remain constant because of the dropping temperature as well as changes in bulk composition owing to the fractional crystallization. The changing bulk magma composition affects some parameters featuring in the saturation equations (e.g. *M* parameter for zircon, see below). In any case the variation in the ESC is likely to be much more limited than for strongly compatible as well as incompatible trace elements (Evans & Hanson 1993).

Any extraneous component in the accessory mineral population (inherited from the source or forming xenocrysts captured from the early assimilated country rocks) would be likely to dissolve at the undersaturated segment of the path *(OM–S)* but would tend to be preserved subsequently *(S–DM)* (Harrison & Watson 1983; Watson & Harrison 1984; Miller et al. 2003).

In reality, the growth of an accessory may deviate considerably from the ideal behaviour, the crystallization being often interrupted by periods of sudden resorption. The reason can be fluctuations in temperature and bulk chemistry of the magma (due to the assimilation/magma mixing) as well as effects of the so-called localized saturation. As proposed by Bacon (1989), non-equilibrium concentration gradients may form adjacent to rapidly growing rock-forming minerals, permitting local crystallization of accessory minerals, even when the bulk chemistry of the magma would rule this out theoretically. However, if the temperature can be assumed to have been approximately constant, and effects of sudden changes in bulk chemistry and localized saturation can be neglected, the saturation models could serve several purposes.

Estimating the liquidus magma temperature

In order to approximate the temperature of magma from which the given accessory mineral crystallized, several assumptions have to be fulfilled:

i. The population of the accessory has *no extraneous component* (inheritance or xenocrysts), as otherwise the obtained temperature would be overestimated. This effect is the most severe for zircon in rather cold, felsic granite suites (Chappell et al. 1998; Miller et al. 2003), many of which have a S-type chemistry (Clemens 2003). The presence of zircon inheritance can be checked using imaging techniques, such as cathodoluminescence or BSE microscopy (Paterson et al. 1992; Hanchar & Miller 1993; Hanchar & Rudnick 1995; Poller 2000; Nasdala et al. 2003). Its impact on saturation calculations can be minimized by corrections employing image analysis or mass balance based on the degree of U–Pb discordance (Broska et al. 1995; Uher et al. 1998; Hanchar & Watson 2003).

ii. The *accessory is distributed homogenously* throughout the igneous body and the *rock composition corresponds to that of the magma*. For instance, the accumulation of zircon crystals, alone or enclosed in other major rock-forming minerals, may dramatically change the Zr concentration of both melt and cumulates. In fact the plutonic rocks very often represent solidified mixtures of a melt and accumulated crystals. Moreover the magma composition may be modified by both assimilation and hybridization processes. However, as discussed by Miller et al. (2003) and demonstrated below, the zircon saturation thermometry is, to a large extent, robust in this respect.

iii. The *accessory mineral crystallized close to the liquidus*, i.e. the given magma batch was saturated early in its history. With care this can be tested by structural evidence, such as the presence of inherited cores in zircons (Fig. 1b–c) or zircon crystals enclosed in early-formed rock-forming minerals. Moreover, the binary plots of a fractionation index versus trace element should be characterized by a negative correlation or, better still, a convex upward trend, indicating that the given accessory started to crystallize (Evans & Hanson 1993; Hoskin et al. 2000) (Fig. 1a). In the latter case, the saturation temperatures for the more basic members of the rock suite (left of the inflection point) would be far below the true liquidus (Piccoli & Candela 1994). On the other hand, the more felsic lithologies beyond the saturation point may yield good estimates of the magma temperatures.

Testing the likelihood of the restitic material survival

In cases when a reliable independent estimate of the magma temperature exists, it can be compared with the temperature obtained by the saturation thermometry. If the 'real' temperature is much lower, some extra component of the accessory mineral must be present, either inherited from the source, or accidental, from assimilated country rocks. In this way it is possible to assess the chance to encounter inherited zircon cores, an information vital for the U–Pb geochronology (e.g. Pidgeon & Aftalion 1978). Care should be exercised in cases when the temperature and/or bulk chemistry of the magma changed suddenly, for instance as a consequence of magma mixing (Elburg 1996; Zeck & Williams 2002; Griffin et al. 2002).

Partial melting

For partial melting, the saturation models enable us to constrain the concentration of the given ESC in the source rocks, prior to and after the melt extraction. Watson & Harrison (1984) have presented scenarios for two conditions of partial melting, related to the concentration of the ESC in the source compared to the saturation level (Fig. 1b–c).

Concentration in the source > saturation level

The melt would be saturated throughout the melting event and its ESC content buffered at a constant level, independent of the degree of melting. The amount of ESC retained by the residue would rise with increasing degrees of the partial melting (Fig. 1b).

Concentration in the source < saturation level

The melt would be saturated in ESC only for a limited time span, until the source is exhausted. As a consequence, the higher still degrees of melting would result in melt batches progressively depleted in the ESC. Low contents of the given ESC observed in a little fractionated magma would have two important corollaries: (1) the parental rocks were probably ESC-poor, and therefore the source was exhausted during melting, resulting in an essentially ESC-free residuum, and (2) no inheritance is likely to be encountered in these intrusions (Fig. 1c).

Kinetic factors

In reality, the dissolution of the accessory minerals is governed by a number of factors, including the temperature, crystal size, the water activity in the magma, diffusivity, absolute solubility of the ESC coupled with the distribution and the degree of undersaturation of the melt. For instance, experiments and numerical modelling show that only very small zircon grains are likely to dissolve during low-temperature anatexis (< 700 °C), while merely relics of large crystals (> 120 μm) are likely to survive a rather hot (850 °C) crustal fusion (e.g. Watson 1996).

The above discussion applies only to equilibrium conditions, given that: 1) the dissolution rate of the accessory was fast relative to the duration of the melting event, 2) the accessory grains in the source were not physically isolated from the melt as inclusions within residual minerals.

In general, the principal factor ruling the kinetics of the zircon, apatite and monazite dissolution seems to be the water activity in the magma. In normal, rather undersaturated and hydrous granitic melts spanning from dehydratation crustal melting, the dissolution of zircon is assumed to be fast enough for the equilibrium to be attained. However, considerably slower dissolution in dry melts (< 2 wt. % H_2O) may pose a major problem (Harrison & Watson 1983; Watson 1996). Monazite and apatite dissolutions are mainly controlled by sluggish LREE and phosphorus diffusion (Harrison & Watson 1984; Rapp & Watson 1986). In dry melts it is much too slow and thus most of the apatite and monazite would fail to equilibrate with the melt. While at elevated water activity the apatite dissolves reasonably quickly, the dissolution of monazite would still take up to several million years — too long compared to the presumed duration of most of the crustal anatectic events (see Spear & Pyle 2002 and references therein). The monazite inheritance is indeed a more common phenomenon than thought previously (Copeland et al. 1988; Harrison et al. 1995; Cocherie et al. 1998).

In the high-grade metamorphic rocks the great majority of the larger accessory mineral grains seem to be located at newly-formed (migrated) grain boundaries of the main rock-forming minerals and thus probably in contact with the partial melt during the anatexis (Watson et al. 1989). In lower-grade rocks the accessories are mostly included in mafic silicates (biotite and/or hornblende) that in course of the dehydratation melting would release them (Clemens 2003). Another factor favouring the dissolution of the accessory phase but difficult to quantify would be the deformation, facilitating a physical fragmentation of the source/residue (Watson & Harrison 1984).

Overview of the saturation formulae

This section gives a synopsis of the saturation formulae. Note that all the temperatures are absolute (K) in accord with most of the original authors (except for Bea et al. 1992).

Zircon

The Zr saturation at a given temperature is defined by the equation of Watson & Harrison (1983):

$$\ln(D_{Zr/melt}) = -3.80 - 0.85\,(M - 1) + \frac{12900}{T} \qquad (1)$$

where:

$D_{Zr/melt}$ = distribution coefficient for Zr between zircon and melt; T = absolute temperature (K); M = cationic ratio

$$\frac{Na + K + 2Ca}{Al.Si} \text{ in the melt.} \qquad (2)$$

Taking into account the theoretical concentration of Zr in stoichiometric zircon (497,644 ppm) and the definition of the distribution coefficient, we can obtain saturation concentrations of Zr (Zr_{SAT}, ppm) by:

$$Zr_{SAT} = \frac{497644}{D_{Zr/melt}}\ . \qquad (3)$$

Computing temperature using the observed Zr concentration:

$$T\,(K) = \frac{12900}{\ln\left(\dfrac{497644}{Zr}\right) + 3.8 + 0.85\,(M - 1)}\ . \qquad (4)$$

Fig. 2a–b shows dependence of the Zr saturation concentrations upon the M parameter and temperature (°C) Eq. (1–3). Especially the Fig. 2b confirms the notion of Miller et al. (2003) that the zircon thermometer is highly resistant to analytical errors in Zr and major-element determinations, as well as the presence of (limited) zircon inheritance. This represents a major advantage of the zircon saturation thermometry for practical applications.

While the inheritance or cumulus zircon would increase the estimated temperature, the crystal accumulation of main rock-forming minerals would have an opposite effect, rendering the temperature estimates too low. Generally speaking, the M value of a mixture between $(1-f)*100$ wt. % liquid (denoted by subscript L) and $f*100$ wt. % crystals (C) is given by (cf. Eq. 2):

$$M = \frac{(1-f)(Na_L + K_L + 2Ca_L) + f(Na_C + K_C + 2Ca_C)}{\left((1-f)Al_L + fAl_C\right).\left((1-f)Si_L + fSi_C\right)}\ . \qquad (5)$$

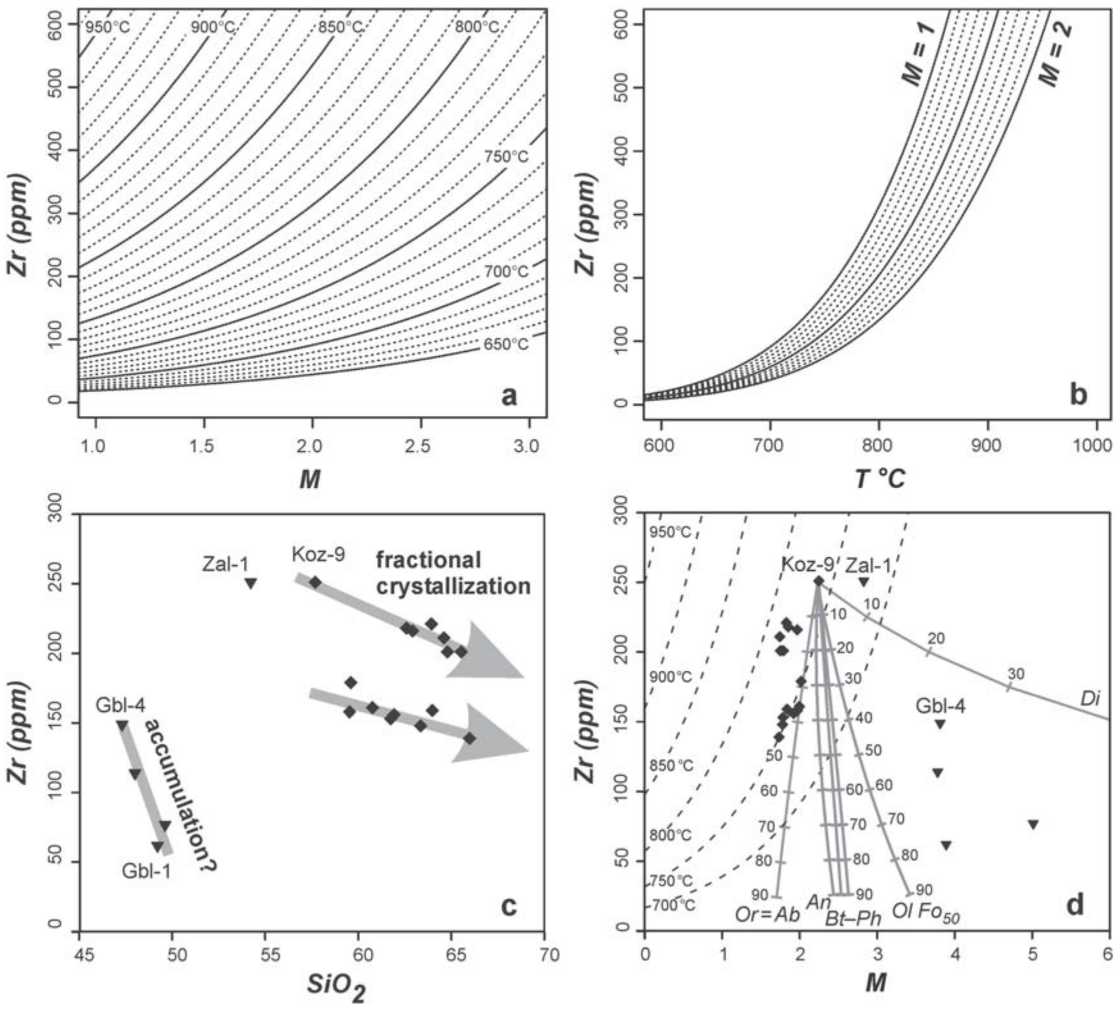


Fig. 2. a–b — Zirconium saturation level (ppm) as a function of cationic ratio M = (Na + K + 2Ca)/(Al.Si) and temperature (°C) (Watson & Harrison 1983). **c** — Binary plot SiO_2 (wt. %)–Zr (ppm) for mainly granodioritic Kozárovice intrusion, Central Bohemian Pluton, and associated monzonitic rocks (Janoušek et al. 2000a,b and unpublished data); shown are also tentative fractionation paths. **d** — Binary plot M vs. Zr (ppm) for the same dataset. Modelled are effects of up to 90 % accumulation of pure mineral phases K-feldspar (Or), albite (Ab), Fe- and Mg-biotite (Bt, Ph), olivine with 50 % of forsterite component (Ol Fo_{50}) and diopside (Di). Assumed initial composition corresponds to the sample Koz-9; theoretical mineral compositions are from Le Maitre (1982).

These effects were examined numerically on a small dataset from the mainly granodioritic Kozárovice intrusion, Central Bohemian Pluton, Czech Republic, and associated monzonitic rocks (Lučkovice and Zalužany: Janoušek et al. 2000a,b and unpublished data). The granodiorites seem to have been saturated in zircon throughout their history (Fig. 2c), forming two groups of zircon saturation temperatures, ~750 °C and ~780 °C (Fig. 2d).

In modelling, initial melt composition corresponding to the sample Koz-9 (Janoušek et al. 2000b) and accumulation of various ideal minerals were assumed (Le Maitre 1982) (Fig. 2d). As shown by simple calculations, the presence of feldspars-rich cumulates would pull the projection points nearly vertically down (typical felsic granitoids: M ~ 1.3, tonalites: M ~ 1.9: Miller et al. 2003; Koz-9: M = 2.25; K-feldspar: M = 1.67; plagioclase: M = 1.67–2.50, increasing with % An). The Ca-rich ferromagnesian minerals with negligible contents of Al_2O_3 (Ca-pyroxenes, Ca-amphiboles) have theoretically very high M (close to infinity as the denominator in Eq. (2) approaches zero) and thus would shift the M of the mixtures strongly to the right (see Di in Fig. 2d). The biotite would be characterized by moderate M (2.57–2.67, only slightly increasing with the Mg contents) and its effect will be similar to that of anorthite.

The Eq. (5) can be used to assess the effects of accumulation of ferromagnesian minerals free of alkalis and calcium ($Na_C + K_C + 2Ca_C = 0$). If also either Si_C or Al_C is zero, the equation changes to:

$$M = \frac{Na_L + K_L + 2Ca_L}{\left((1-f)Al_L + fAl_C\right)Si_L} \quad \text{or} \quad M = \frac{Na_L + K_L + 2Ca_L}{Al_L\left((1-f)Si_L + fSi_C\right)} \tag{6}$$

with limits

$$\lim_{f \to 1}(M) = \frac{Na_L + K_L + 2Ca_L}{Al_C\, Si_L} \quad \text{and} \quad \lim_{f \to 1}(M) = \frac{Na_L + K_L + 2Ca_L}{Al_L Si_C}$$

respectively, leading to:

$$\lim_{f\to 1}(M) = \frac{Al_L}{Al_C} M_L \quad \text{if } Si_C = 0 \text{ and} \tag{7}$$

$$\lim_{f\to 1}(M) = \frac{Si_L}{Si_C} M_L \quad \text{if } Al_C = 0. \tag{8}$$

Thus for Ca-poor pyroxenes (En, Fs: Si = 0.5, Al = 0) and Koz-9 as a melt composition the theoretical intersection with the x axis (Eq. 8) would be 2.44, i.e. the points would be shifted nearly vertically. For minerals with lower Si (e.g. olivine, Si = 0.33, Al = 0) the intersection would be further right (3.66).

Even though the results of such a numerical modelling should be viewed with caution, as there is unfortunately a dearth of experimental data for compositions other than rhyolite glasses (Hanchar & Watson 2003), moderate accumulation of albite and K-feldspar would have little effect on the calculated saturation temperatures for normal granitic compositions. The projection points simply move more or less parallel to the isotherms. On the other hand, accumulation of Ca-rich ferromagnesian minerals (diopsidic pyroxene or magnesiohornblende) may have pronounced effects even if as little as ~10 % of the cumulate is present.

Monazite

Monazite saturation temperature as a function of the LREE concentration and water activity is defined by (Montel 1993):

$$T(K) = \frac{13318}{9.5 + 2.34\,D + 0.3879\sqrt{H_2O} - \ln(REE_t)} \tag{9}$$

where:

$$D = \textit{cationic ratio } 100\,\frac{Na + K + Li + 2Ca}{Al}\,\frac{1}{Al + Si}\,; \tag{10}$$

$$REE_t = \frac{\sum \frac{REE_i}{at.weight_i}}{Xmz} \quad \text{for } La, Ce, Pr, Nd, Sm \text{ and } Gd;$$

Xmz = mole fraction of the REE-phosphates in monazite;
H_2O = assumed water content in the magma.

Apatite

Saturation P_2O_5 concentration

For metaluminous rocks ($A/CNK \leq 1$):

The saturation level of P_2O_5 according to Harrison & Watson (1984) (P_2O_5HW) is calculated using a combination of the expressions:

$$\ln(D_P) = \frac{8400 + 26400(\mathrm{SiO_2} - 0.5)}{T} - 3.1 - 12.4(\mathrm{SiO_2} - 0.5)$$

and (11)

$$P_2O_5HW = \frac{42}{D_P} \tag{12}$$

where:
T = absolute temperature (K); D_P = distribution coefficient for phosphorus between apatite and melt; $\mathrm{SiO_2}$ = weight fraction of silica in the melt (wt. % $\mathrm{SiO_2}/100$).

For peraluminous rocks ($A/CNK > 1$):

The P_2O_5 concentrations obtained according to the model of Harrison & Watson (1984) (P_2O_5HW, see above) can be corrected for higher phosphorus solubility in the peraluminous melts by the following equations:

$$P_2O_5 = P_2O_5HW e^{\frac{6429(ACNK - 1)}{T - 273.15}} \tag{13}$$

(Bea et al. 1992)

$$P_2O_5 = P_2O_5HW + (A/CNK - 1)\, e^{\frac{-5900}{T} - 3.22\mathrm{SiO_2} + 9.31} \tag{14}$$

(Pichavant et al. 1992).

Apatite saturation temperatures

For metaluminous rocks ($A/CNK \leq 1$):

$$T(K) = \frac{8400 + 26400(\mathrm{SiO_2} - 0.5)}{\ln\left(\frac{42}{P_2O_5}\right) + 3.1 + 12.4(\mathrm{SiO_2} - 0.5)} \tag{15}$$

(Harrison & Watson 1984).

For peraluminous rocks ($A/CNK > 1$):

From equations (11–13) we obtain an expression that needs to be solved for T (in K) by iterations:

$$P_2O_5 = 42e^{\frac{6429(\mathrm{ACNK} - 1)}{T - 273.15} - \frac{8400 + 26400(\mathrm{SiO_2} - 0.5)}{T} + 3.1 + 12.4(\mathrm{SiO_2} - 0.5)} \tag{16}$$

(Bea et al. 1992)

as is the formula spanning from Eqs. (11), (12) and (14):

$$P_2O_5 = \frac{42}{e^{\frac{8400 + 26400(\mathrm{SiO_2} - 0.5)}{T} - 3.1 - 12.4(\mathrm{SiO_2} - 0.5)}} + (A/CNK - 1)e^{\frac{-5900}{T} - 3.22\,\mathrm{SiO_2} + 9.31} \tag{17}$$

(Pichavant et al. 1992).

In Fig. 3a–b is shown dependence of the P_2O_5 saturation levels (Harrison & Watson 1984) on temperature and $\mathrm{SiO_2}$. At the first glimpse it is obvious that the apatite saturation thermometry for metaluminous, more siliceous compositions is extremely sensible to apatite accumulation or even small errors in the P_2O_5 determinations.

However, the melts with A/CNK > 1 were shown to be capable of dissolving much more apatite than predicted by the formula of Harrison & Watson (1984). The reason therefore is origin of aluminium phosphate complexes in peraluminous aluminosilicate melts, in which P^{5+} is

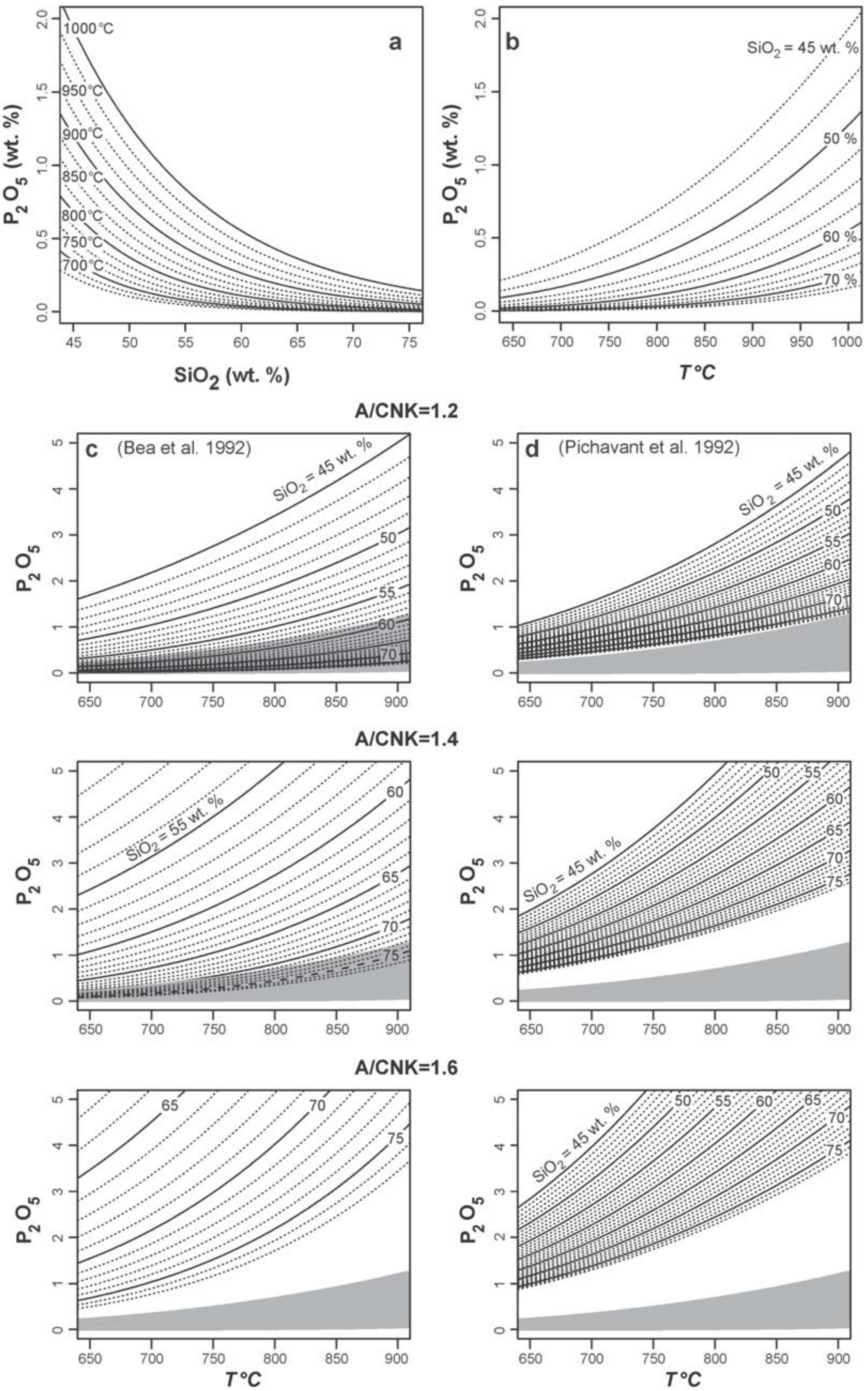


Fig. 3. a–b — Phosphorus saturation level (wt. % P_2O_5) as a function of SiO_2 (wt. %) and temperature (°C) (Harrison & Watson 1984). **c–d** — Saturation levels for peraluminous rocks with A/CNK = 1.2, 1.4 and 1.6 corrected according to Bea et al. (1992, left column) and Pichavant et al. (1992, right column). Shaded field denotes a range for metaluminous rocks with the same silica content (SiO_2 = 45–77 wt. %: Harrison & Watson 1984).

bonded with Al^{3+} to form $AlPO_4$ species (Mysen et al. 1999 and references therein). These effects are shown in Fig. 3c–d for the two most elaborated models, published by Bea et al. (1992) and Pichavant et al. (1992). The latter seems to give solubilities significantly lower than the former. Wolf & London (1994) found the phosphorus solubility to be linearly dependent on the A/CNK values:

$$P_2O_5 = -3.4 + 3.1 * A/CNK \tag{18}$$

However, their experiments were conducted only at a single temperature (T = 750 °C).

The apatite thermometry in felsic, strongly peraluminous melts is furthermore flawed by the fact that feldspars can incorporate large amounts of phosphorus via a berlinite substitution (e.g. London et al. 1990). In Ca-poor magmas plagioclase would crystallize early, further increasing the P/Ca ratio in the melt. In extreme cases of low-T, highly fractionated, Ca-poor and strongly peraluminous magmas, the formation of aluminium phosphate complexes may prohibit the apatite saturation completely, with all phosphorus being allocated to other phosphates and/or feldspars (Piccoli & Candela 2002). The calculated apatite saturation temperatures in these cases would be of course meaningless.

Saturnin: a R language script for saturation calculations

System overview

To the author's knowledge, a flexible and comprehensible tool that would perform all the necessary saturation calculations has so far been lacking. As shown by Janoušek (2000) and Grunsky (2002), the freeware R language (R Development Core Team, 2003) [1] is an ultimate environment for writing geochemical recalculation and plotting routines that are compact and platform independent. Within this rich environment, a set of scripts, called *Saturnin*, has been developed. They have been included, in a slightly modified form, as a plugin for the larger system called *GCDkit for Windows* (Janoušek et al. 2003) [2]. The scripts have been tested in R for Windows, version 2.1.1. They should run not only under Windows 9x/2000/NT/XP (higher versions are strongly recommended) but also, theoretically nearly without modifications, on Mac OS X or Linux.

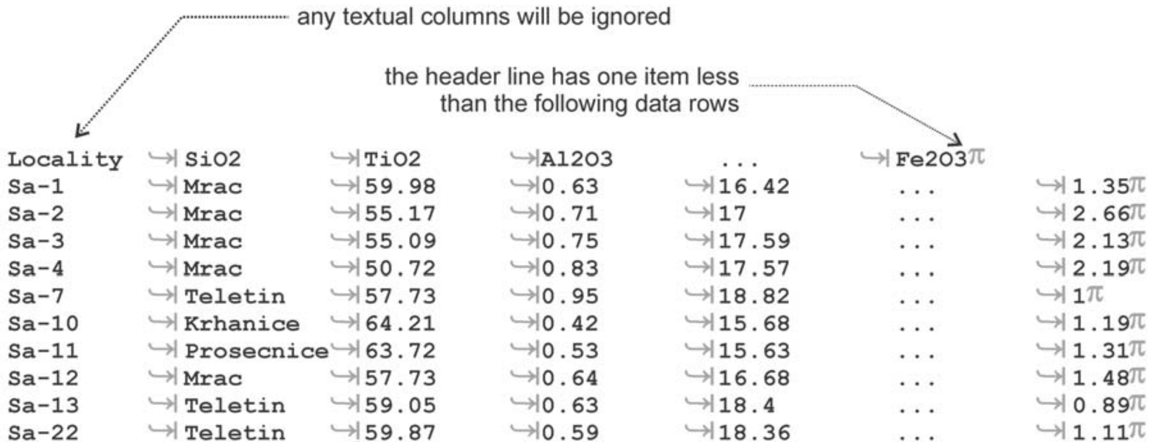
Obtaining, installing and running Saturnin

If not present already, the R environment needs to be installed first from the nearest mirror [1]. For Windows, a complete distribution is packed in a single file *'R-X.X.X-win32.exe'*, where X.X.X is the version number (e.g. *R-2.2.1-win32.exe*). Run the executable file and select the required items as well as the target directory.

The second step would be to download a single text file with the code of *Saturnin* from [3], the Geologica Carpathica Web page [4] or request it by email from the author. In Windows, the code is started by invoking the *File|Source R code* command from the RGUI menu, in other systems using the standard R command *source*. It might be wise to change the working directory, in Windows invoking the menu item *File|Change dir...*, otherwise using the R command *setwd*:

```
setwd("c:/data")
```

The programme requires plain text (ASCII) files in which each row represents one sample and individual items (major and minor elements, Zr, and, or LREE concentrations) are in columns delimited by tabulators (Fig. 4). The first line contains labels for the data columns (except that for the first column that is automatically assumed to contain the sample names). The first row therefore should have one item less than all the following ones. The columns can be given in an arbitrary order, missing values (replaced in R by 'NA', standing for 'not available') for elements/oxides not directly involved in the calcula-



any textual columns will be ignored

the header line has one item less than the following data rows

```
Locality ⇥SiO2       ⇥TiO2    ⇥Al2O3     ...      ⇥Fe2O3π
Sa-1     ⇥Mrac       ⇥59.98   ⇥0.63    ⇥16.42     ...     ⇥1.35π
Sa-2     ⇥Mrac       ⇥55.17   ⇥0.71    ⇥17        ...     ⇥2.66π
Sa-3     ⇥Mrac       ⇥55.09   ⇥0.75    ⇥17.59     ...     ⇥2.13π
Sa-4     ⇥Mrac       ⇥50.72   ⇥0.83    ⇥17.57     ...     ⇥2.19π
Sa-7     ⇥Teletin    ⇥57.73   ⇥0.95    ⇥18.82     ...     ⇥1π
Sa-10    ⇥Krhanice   ⇥64.21   ⇥0.42    ⇥15.68     ...     ⇥1.19π
Sa-11    ⇥Prosecnice⇥63.72    ⇥0.53    ⇥15.63     ...     ⇥1.31π
Sa-12    ⇥Mrac       ⇥57.73   ⇥0.64    ⇥16.68     ...     ⇥1.48π
Sa-13    ⇥Teletin    ⇥59.05   ⇥0.63    ⇥18.4      ...     ⇥0.89π
Sa-22    ⇥Teletin    ⇥59.87   ⇥0.59    ⇥18.36     ...     ⇥1.11π
```

the columns are separated by tabulators, no fixed order of individual variables is required

Fig. 4. Example of a tab-delimited text file formatted for *Saturnin*.

tions are allowed. However, column names must have simple form to be treated properly by automatic routines (i.e. 'SiO2' instead of 'SiO2 [wt. %]' etc.) and must be unique, as must be the sample names. When a data set is loaded into the system, all numerical data should be allocated in a data frame '*WR*' as follows:

```
load.file()
```

Generally speaking, the functions in R can be called simply by typing their names with required parameters in parentheses. If some of the parameters are omitted, defaults from the function's definitions are taken:

```
zr.saturation(T=850)
zr.saturation()
x<-c(3,3,3,2.5,2,2,7,3)
# assuming 8  samples
mz.saturation(H2O=x)
```

The results of calculations are printed on the screen and stored in a matrix/vector *'results'*.

In Windows, this variable can be subsequently copied to a clipboard using the function *r2clip:*

```
r2clip()
```

and pasted into any other programme, such as MS Excel, for further processing. Note that all temperatures in the output have been converted to the centigrade (°C).

Conclusions

1 — Zircon saturation thermometer is rather robust to analytical errors, presence of minor inheritance, as well as moderate accumulation of feldspars and some ferromagnesian minerals (Ca-poor pyroxenes, to a lesser extent olivine). On the other hand, addition of Ca-rich pyroxene or Ca-rich amphibole cumulate renders quickly the calculated temperatures too low.

2 — Apatite saturation thermometry is a poor tool for felsic metaluminous rocks, being exceedingly sensitive to small analytical errors in the phosphorus determination as well as the presence of extraneous apatite. An even stronger element of uncertainty is added for peraluminous lithologies, when the increased apatite solubility is poorly constrained by the current models and where other P-bearing minerals, most importantly feldspars and monazite, come to the play.

3 — *Saturnin* is a newly developed software that performs otherwise rather tedious zircon, monazite and apatite saturation calculations in igneous geochemistry. It is written in a freeware R language and designed to be platform independent. While the Windows users would probably find it easier to access the programme as a part of the larger package *GCDkit (http://www.gla.ac.uk/gcdkit)*, on Macintosh and Linux it can be invoked as a stand-alone application.

4 — The programme can be downloaded from the WWW or can be obtained upon request from the author, who hopes that it will promote the power and beauty of the R language in a wider geochemical community.

Acknowledgments: This manuscript originated during the research stay of VJ at the Institute of Mineralogy, University of Salzburg, in the framework of the FWF Project 15133-GEO (to Fritz Finger). Generous support from the Czech Grant Agency (GAČR 205/03/0040) is gratefully acknowledged. The author is indebted to the R Core Team and other people from the R community for their efforts in continuous developing R. The paper benefited from helpful reviews by Igor Petrík and two anonymous colleagues. The author also thanks Igor Broska (Academy of Sciences, Bratislava) for organizing a workshop explaining the principles of saturation calculations, Fritz Finger for comments on an early version of the manuscript, Colin Farrow (University of Glasgow) and Vojtěch Erban (Czech Geological Survey, Prague) for interesting discussions about the R language. Vojtěch Erban also helped considerably by testing the code. Moreover, Angela Storkey (La Trobe University, Bundoora, Australia) assisted with painstaking debugging of the complex apatite saturation script.

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Appendix: saturnin.r – programme code

[See *http://www.gla.ac.uk/gcdkit/saturnin/saturnin.pdf* for detailed documentation]

Auxiliary functions

```
require(”MASS”)
major<-c(”SiO2”,”TiO2”,”Al2O3”,”Fe2O3”,”FeO”,”MnO”,”MgO”,
 ”CaO”,”Na2O”,”K2O”,”P2O5”,”Li2O”)
LREE<-c(”La”,”Ce”,”Pr”,”Nd”,”Sm”,”Gd”)
WR<-data.matrix(0)

# Loading data file
load.file<-function(){
  if(.Platform$OS.type==”windows”){
    filename<-file.choose()
  }else{
    filename<-readline(”Enter the filename: ”)
  }
  x<-read.table(filename,sep=”\t”,dec=”.”,
   check.names=F, fill=T) # For decimal commas: dec=”,”
  # Ensures that all the necessary variables are there,
  # even if empty
 add.on<-function(param,what){
    if(any(colnames(WR)==param))return(WR)
    options(show.error.messages = F)
    try(WR<-cbind(WR,what))
    try(colnames(WR)[ncol(WR)]<-param)
    options(show.error.messages = T)
    return(WR)
  }
  col.names<-c(major,LREE,”Zr”)
  y<-matrix(nrow=nrow(x),ncol=length(col.names),
   dimnames=list(rownames(x),col.names))
  WR<-cbind(x,y[,setdiff(colnames(y),colnames(x))])
  WR<-add.on(”Li2O”,WR[,”Li”]/0.46452/1e4)
  # Recalculates Li (ppm) to LiO2 (wt%) if necessary
  WR<-add.on(”FeO”,WR[,”FeOt”])
  WR<-add.on(”FeO”,WR[,”FeO*”])
  WR<-add.on(”A/CNK”,acnk(millicat(WR)))
  WR[WR<=0]<-NA # Missing values
  print(WR)
  WR<<-WR
  return(WR)
}
```

```
# Calculates millications
millicat<-function(what=WR){
  MW<c(60.0848,79.8988,101.96128,159.6922,71.88464,70.9374,
    40.3044,56.0794,61.97894,94.1954,141.94452,29.8814)
  # Molecular weights for ’major’
  names(MW)<-major
  fact<-c(1,1,2,2,1,1,1,1,2,2,2,2)
  # Number of cations per molecule
  names(fact)<-major
  z<-t(apply(what[,major],1,function(x){x/MW[major]*
    fact[major]*1000}))
  return(z)
}
# Calculates A/CNK
acnk<-function(what){
  z<-what[,”Al2O3”]/(what[,”Na2O”]+what[,”K2O”]+
    2*what[,”CaO”])
  return(z)
}
# Normalizes a matrix to a given sum
normalize2total<-function(what,total=100){
  z<-t(apply(what,1,function(x,y){x/sum(x,na.rm=T)*y},
    y=total))
  return(z)
}
# Filters out from matrix ‘where’ rows in which exist all columns
specified in ‘what’
filter.out<-function(where,what){
  i<-apply(where[,what]),1,function(x){all(!is.na(x))})
  z.names<-rownames(where)[i]
  z<-as.matrix(where[i,what])
  rownames(z)<-z.names
  colnames(z)<-what; mode(z)<-”numeric”
  return(z)
}
r2clip<-function(what=results){
  if(is.null(what)) stop(”No data available!”)
  filename<-file(”clipboard”,open=”w”)
  what<-as.matrix(what)
  if(ncol(what)==1)colnames(what)<-””
  write.matrix(cbind(rownames(what),what),filename,sep=”\t”)
  close(filename)
}
```

Zircon saturation

Parameters:

cats	numeric matrix; whole-rock data recast to millications
T	assumed magma temperature (default = 750 °C)
Zr	vector with Zr concentrations (ppm)

Returns a matrix ‘results’ with the following columns:

M	cationic ratio (Eq. 2)
Zr	observed Zr concentrations (ppm) (Eqs. 1–3)
TZr.sat.C	zircon saturation temperatures (°C) (Eq. 4)

```
zr.saturation<-function(cats=millicat(WR),T=750,
 Zr=subset(WR, Zr>0, ”Zr”)){
  T<-T+273.15
  cats<-cats[rownames(Zr),]
  x<-normalize2total(cats)
  M<-(x[,”Na2O”]+x[,”K2O”]+2*x[,”CaO”])/(x[,”Al2O3”]*
   x[,”SiO2”])*100
  DZr1<-exp(-3.8-0.85*(M-1)+12900/T)
  Zr.sat<-497644/DZr1
  DZr<-497644/Zr
  TZr.sat.C<-12900/(log(DZr)+3.8+0.85*(M-1))-273.15
  y<-cbind(M,Zr,round(Zr.sat,1),round(TZr.sat.C,1))
  colnames(y)<-c(”M”,”Zr”,”Zr.sat”,”TZr.sat.C”)
  results<<-y
  return(y)
}
```

Monazite saturation

Parameters:

cats	numeric matrix; whole-rock data recast to millications
H2O	assumed water contents of the magma (default = 3 wt. %)
Xmz	mole fraction of the REE-phosphates in monazite (default = 0.83)

Returns a matrix ‘results’ with the following columns:

Dmz	cationic ratio (Eq. 10)
Tmz.sat.C	monazite saturation temperature (°C) (Eq. 9)

```
mz.saturation<-function(cats=millicat(WR),H2O=3,
  Xmz=0.83){
  MW.REE<-c(138.9055,140.12,140.9077,144.24,151.4,
   154.25)# Atomic weights for LREE
  names(MW.REE)<-LREE
  REE<-filter.out(WR,LREE)
  cats<-cats[rownames(REE),]
  # Get only samples for which all LREE are available
  ree<-t(t(REE)/MW.REE)
  reex<-apply(ree,1,sum,na.rm=T)/Xmz
  x<-normalize2total(cats,100)
  D<-(x[,”Na2O”]+x[,”K2O”]+2*x[,”CaO”])/x[,”Al2O3”]*
   1/(x[,”Al2O3”]+x[,”SiO2”])*100
  T.calc<-13318/(9.5+2.34*D+0.3879*sqrt(H2O)-log(reex))
   -273.15
  y<-cbind(D,round(T.calc,1))
  colnames(y)<-c(”Dmz”,”Tmz.sat.C”)
  results<<-y
  return(y)
}
```

Apatite saturation

Parameters:

Si	SiO_2 contents in the melt (wt. %)
ACNK	vector with A/CNK (mol %) values
P2O5	vector with P_2O_5 concentrations (wt. %)
T	assumed magma temperature (default = 750 °C)

Returns a matrix ‘results’ with the following columns:

A/CNK	A/CNK values
Tap.sat.C.H+W	saturation T of Harrison & Watson (1984) (°C) (Eq. 15)

For peraluminous rocks (A/CNK > 1) also:

Tap.sat.C.Bea	saturation T of Bea et al. (1992) (°C) (Eq. 16)
Tap.sat.C.Pich	saturation T of Pichavant et al. (1992) (°C) (Eq. 17)

```
ap.saturation<-function(Si=WR[,”SiO2”],
 ACNK=WR[,”A/CNK”],P2O5=data.matrix(WR)[,”P2O5”],T=750){
  Si<-Si/100
  T<-T+273.15
  # Harrison and Watson (1984)
  A<-8400+(Si-0.5)*26400
  B<-3.1+12.4*(Si-0.5)
  D.HW<-exp(A/T-B)
  P2O5.HW<-42/D.HW
  T.HW<-A/(log(42/P2O5)+B)-273.15
  # A general routine that solves non-linear equation
  # for T (deg C) by bisection method
  solve.T<-function(fun,tmin=0,tmax=NULL){
    T.calc<-NULL
    for(i in 1:length(Si)){
      if(ACNK[i]>1){
      ttold<-0;tt<-1
      if(is.null(tmax))tt.max<-T.HW[i]+273 else
       tt.max<-tmax
        # H+W temperature is a feasible max. estimate
      tt.min<-tmin
      while(abs(ttold-tt)>0){
        ttold<-tt
        tt<-(tt.max-tt.min)/2+tt.min
        expr<-gsub(”Si”,Si[i],fun)
        expr<-gsub(”ACNK”,ACNK[i],expr)
        expr<-gsub(”T”,tt,expr)
        pp<-eval(parse(text=as.expression(expr)))
        if(pp>P2O5[i])tt.max<-tt else tt.min<-tt
      }
        T.calc[i]<-tt
      }else{
        T.calc[i]<-NA
      }
    }
  return(T.calc-273.15)
  }
# Pichavant et al. (1992)
  T.PV<-solve.T(”42/exp((8400+(Si-0.5)*26400)/T-3.1-
   12.4*(Si-0.5))+(ACNK-1)*exp(-5900/T-3.22*Si+9.31)”)
# Bea et al. (1992)
  T.Bea<-solve.T(”42*exp(((ACNK-1)*6429)/(T-273.15)-
   (8400+(Si-0.5)*26400)/T+3.1+12.4*(Si-0.5))”)
  y<-cbind(T.HW,T.Bea,T.PV);y<-round(y,1)
  y<-cbind(round(ACNK,2),y)
  colnames(y)<-c(”A/CNK”,”Tap.sat.C.H+W”,
   ”Tap.sat.C.Bea”,”Tap.sat.C.Pich”)
  rownames(y)<-names(P2O5)
  results<<-y
  return(y)
}
```