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Rb-Sr and U-Pb age dating of granite rocks by inductively coupled plasma mass spectrometry

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Inductively coupled plasma-mass spectrometry (ICP-MS) was used as alternative to thermal ionization mass spectrometer (TIMS) for age dating of granite samples originating from different magmatic volcanic rock formations on the Arabian shield. Cation exchange chromatography was used to avoid isobaric overlap of ^{87}Rb with ^{87}Sr and ^{204}Hg with ^{204}Pb ions signals to the largest possible extent, while mathematical correction was applied to correct for the remaining interference. Sr was separated from its matrix using a crown ether-Eichrom's Sr resin. Pb separated from its matrix by developing a method using a crown ether-Eichrom's Sr resin. The accuracy of the method developed was evaluated by means of isotopic analysis of strontium carbonate SRM-987 and common lead SRM-981 isotopic standards from NIST. Precisions of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios measurements are $\leq 0.1\%$ and 0.3% (1σ), respectively. Overall, this case study shows the merits of ICP-MS for exploratory age determinations and studies of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios which can differentiate between magmatic origin of granite.

Key words: age dating / ICP-MS / granite / U-Pb / Rb-Sr.

INTRODUCTION

The discovery of radioactivity demonstrated that radioactive atoms transmute into atoms at predetermined and essentially constant rates, provided the basis for a new clock to measure geological time. The ability to quantify time is very important for geologists trying to determine the chronology and rate of various processes (Miller et al., 2003; Jahn et al., 1999; Hecht et al., 1999; Hekinian et al., 1999; Böhn et al., 1999; Gao and Klemm, 2003). Traditionally, thermal ionization mass spectrometry, usually with multiple ion or faraday collectors, (MC-TIMS) is used for Rb/Sr and U/Pb geochronology (Paquette et al., 2003; Birck, 2001; Heumann et al., 1995; Potter et al., 2005; Black et al., 2004) because most applications require a precision (analytical repeatability) of better than 0.01% relative standard deviation (RSD) of the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios. Such precision can also be achieved with ICP-MS using multiple ion collectors (MC-ICP-MS) (Potter et al., 2005; Balcaen et al., 2005; Waight et al., 2002; Burton et al., 2002; Ehrlich et al.,

2001). For example, Waight et al. (2002) measured the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in whole rock volcanic samples with a precision of 0.003–0.005% (2σ). However, for several applications, ICP-MS with single ion collectors has also been successfully applied for precise Sr and Pb isotope ratio measurements Furuta, 1991; Ketterer et al., 1991; Ketterer, 1992; Koirtjohann, 1994; Xie and Kerrich, 1995; Begley and Sharp, 1997; Quétel et al., 1997; Heumann et al., 1998; Vanhaecke et al., 1999; Prohaska et al., 2002; Vanhaecke et al., 2001; Vanhaecke et al., 1999; Zoriy et al., 2003. The precision for the determination of Sr isotope ratios by quadrupole-based ICP-MS is limited to approximately 0.1% RSD (Vanhaecke et al., 1999). Using double-focusing sector field ICP-MS (at low mass resolution) a precision of 0.064% RSD ($n = 5$) has been reported (Vanhaecke et al., 2001). However, for applications for which the ultimate level of precision is not required, Quadrupole-based Inductively coupled Plasma Mass Spectrometer (ICP-QMS) is an attractive alternative to TIMS, owing to its ease of operation, the widespread availability of ICP-QMS instruments and the much higher sample throughput. Highly favorable cases for ICP-QMS are preliminary

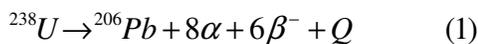
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dating or isotopic screening studies of rock series in which the expected variation of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios exceeds 1% as a result of a combination of relatively great age (>50 Ma) and large variations of the Rb/Sr and U/Pb ratios.

In order to avoid isobaric interference of ^{87}Rb with ^{87}Sr or ^{204}Hg with ^{204}Pb , a strontium or lead separation from digested samples by extraction chromatography is the method of choice or by the application of the collision-induced reaction in a dynamic reaction cell (DRC) of ICP-MS. For example, Moens et al. (2001) used ion-molecule selective reactions of Sr^+ with CH_3F in a DRC-ICP-MS to eliminate the isobaric interference of $^{87}\text{Rb}^+$ on $^{87}\text{Sr}^+$ by measuring the intensities of the corresponding SrF^+ ion beams. This approach works because Rb is unreactive with CH_3F . The precision obtained for the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurement was 0.03%. Laser ablation (LA) ICP-MS has been increasingly used in recent years (Potter et al., 2005; Wang et al., 2006; Woodhead et al., 2005), which allows for the direct analysis of solid samples without sample preparation, microlocal analysis with low detection limits, and the determination of precise isotopic ratios. Thus, Prohaska et al. (2002) investigated prehistoric human bones and teeth using LA-ICP-MS with a sector field instrument and obtained a 0.1–0.2% RSD precision for $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio measurements in these samples. However, accurate Sr isotope ratio measurements are only possible if the Rb content is very low in comparison to the Sr concentration, otherwise separation prior to measurement is required.

Methods of dating

Calculation details of Rb-Sr method of dating was reported in Vanhaecke et al. (1999). In the following we describe ^{238}U - ^{206}Pb method of dating. The growth of radiogenic ^{206}Pb in mineral can be described by an equation derivable from the law of radioactivity.



The total number of atoms ^{206}Pb in a rock or mineral, whose age is t , is obtained from the following equation:

$$^{206}\text{Pb} = ^{206}\text{Pb}_i + ^{238}\text{U} (e^{\lambda t} - 1) \quad (2)$$

where ^{206}Pb is the total number of atoms of this isotope in a unit weight of the minerals at the present time; $^{206}\text{Pb}_i$ is the number of atoms of this isotope that was incorporated into the unit weight of the minerals at the time of its formation; ^{238}U is the number of atoms of this isotope in a unit weight of the mineral at the present time; λ is the decay constant of ^{238}U in unit of reciprocal years ($\lambda_{238} = 1.55 \times 10^{-10} \text{ a}^{(33)}$); and t is the time elapsed in years since the time of formation of the minerals, that is, t is the “age” of the mineral. We can modify Equation (2) by dividing each term by the number of ^{204}Pb atoms, which

constant because this isotope is stable and is not produced by decay of a naturally occurring isotope of another element. Thus we obtain the following equation:

$$\frac{^{206}\text{Pb}}{^{204}\text{Pb}} = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_i + \frac{^{238}\text{U}}{^{204}\text{Pb}} (e^{\lambda t} - 1) \quad (3)$$

this equation is the basis for age determinations by the ^{238}U - ^{206}Pb method. Equation (3) is valid only when the number of ^{206}Pb and ^{238}U atoms in the minerals have changed as a result of radioactive decay. Equation (2) can be solved for t :

the numerical value of t is a “date” in the geological past. This date is the “age” of the mineral only when that mineral has remained a closed system with respect to ura-

$$t = \frac{1}{\lambda} \ln \left[\frac{\frac{^{206}\text{Pb}}{^{204}\text{Pb}} - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_i}{\frac{^{238}\text{U}}{^{204}\text{Pb}}} + 1 \right] \quad (4)$$

nium and lead, when the assumed value of the initial $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is appropriate, and when the analytical results are accurate and representative of the material to be dated.

$^{238}\text{U}/^{204}\text{Pb}$ Calculations

The ratio of the concentrations of U to Pb is converted into the $^{238}\text{U}/^{204}\text{Pb}$ ratio by the following equation:

where $^{238}\text{U}/^{204}\text{Pb}$ is the ratio of these isotopes in terms of numbers of atoms present in a unit weight of the mineral at the present time, (U/Pb) is the ratio of the concentrations of these elements, $\text{Ab}(^{238}\text{U})$ and $\text{Ab}(^{204}\text{Pb})$

$$\frac{^{238}\text{U}}{^{204}\text{Pb}} = \left(\frac{\text{U}}{\text{Pb}} \right) \times \frac{\text{Ab}(^{238}\text{U})}{\text{Ab}(^{204}\text{Pb})} \times \frac{W(\text{Pb})}{W(\text{U})} \quad (5)$$

are the isotopic abundances of ^{238}U and ^{204}Pb , respectively, and $W(\text{U})$ and $W(\text{Pb})$ are the respective atomic weight. Note that the abundance of ^{204}Pb and the atomic weight of lead depend on the abundances of ^{206}Pb , ^{207}Pb , and ^{208}Pb and therefore appropriate values must be calculated for each sample, as follows:

$$\text{Ab}(204) + \text{Ab}(206) + \text{Ab}(207) + \text{Ab}(208) = 1 \quad (6)$$

$$\left. \begin{aligned} \frac{\text{Ab}(208)}{\text{Ab}(204)} &= R_{208} \\ \frac{\text{Ab}(207)}{\text{Ab}(204)} &= R_{207} \\ \frac{\text{Ab}(206)}{\text{Ab}(204)} &= R_{206} \end{aligned} \right\} \text{measured by ICP-MS} \quad (7)$$

Rearrangement of equations (6) and (7) leads to equation (8):

$$Ab(204) = \frac{1}{(1 + R_{208} + R_{207} + R_{206})} \quad (8)$$

using the calculated $Ab(^{204}Pb)$ in equation (8), the abundances of the lead isotopes in a sample are calculate as:

$$Ab(^{208}Pb) = \frac{^{208}Pb}{^{204}Pb} * Ab(^{204}Pb) = R_{208} * Ab(^{204}Pb) \quad (9)$$

$$Ab(^{207}Pb) = \frac{^{207}Pb}{^{204}Pb} * Ab(^{204}Pb) = R_{207} * Ab(^{204}Pb) \quad (10)$$

$$Ab(^{206}Pb) = \frac{^{206}Pb}{^{204}Pb} * Ab(^{204}Pb) = R_{206} * Ab(^{204}Pb) \quad (11)$$

The molecular weight of Pb calculated as:

$$W(Pb) = 203.973020Ab(^{204}Pb) + 205.97444Ab(^{206}Pb) + 206.975871Ab(^{207}Pb) + 207.976627Ab(^{208}Pb) \quad (12)$$

Experimental

Reagents: Only high purity reagents were used in the preparation of the sample solutions. Doubly distilled water of 18 M Ω cm was obtained by purifying system (Barnstead/Thermolyne, Iowa, USA). HNO₃, H₂ClO₄, HCl and HF (analytical grade) was purchased from Romil LTD, Cambridge, UK. A multielement standard solution from Merck was used for trace element determination.

Samples and Mineral Separation: About 400 g of bulk granite samples were gathered from the Arabian shield (Shammar and Afif areas) crushed in a jaw crusher and then in a disk mill, and the samples were sieved to isolate the 150–250 μ m size. Mineral separation was achieved by utilizing contrasts in the densities and magnetic properties of the various minerals. Na polytungstate was mixed with water to provide a range of liquid densities that bracketed the various minerals. Density separates were then further purified using a Carpco magnetic separator (WHIMS 3x4L). Granite samples and separated fractions were investigated by X-ray diffraction (Bruker D8 Advance, Germany).

Strontium separation: The sample materials are taken into solution by open vessel acid digestion on a hotplate. 0.5 g of powdered sample was dissolved using 10ml HF and 4 ml HClO₄ in a PTFE vessel. After evaporation to dryness, the residue was taken up in 10 ml 2M HNO₃. Subsequently, Sr was isolated from the matrix components and from Rb. The latter is required to avoid isobaric overlap of the signals of ⁸⁷Sr⁺ and ⁸⁷Rb⁺ and also other potential interferences with ⁸⁶Sr and ⁸⁷Sr, as shown in Table 1. Often, cation-exchange chromatography (Vanhaecke et al., 2001) is used for this purpose. In this work however, Sr was isolated using a dedicated and commercially available crown ether-based Sr resin (Horwitz et al., 1992). Columns loaded with this Sr resin material were purchased from Eichrom Technologies Inc. (Bruz, France). The resin is based on the crown ether di-tert-butyl-cyclohexano-18-crown-6, dissolved in octan-1-ol and sorbed onto an inert polymethacrylate, with a particle size between 100 and 150 μ m. The maximum column load is 2 ml. The method involves passage of the sample solution in 2M HNO₃ medium through the extraction column, which retains Sr. Rubidium and other matrix elements are washed from

the column leaving a pure Sr fraction on-column. The Sr may then be stripped from the column with a small volume of distilled water. The wall procedure was done without sample and used as blank. A typical elution curve for Rb and Sr thus obtained is given in Figure 1.

Lead separation (Weiss et al., 2004): The sample materials are taken into solution by open vessel acid digestion on a hotplate. 0.5 g of powdered sample was dissolved using 10ml HF and 4 ml HClO₄ in a PTFE vessel. After evaporation to dryness, the residue was taken up in 10 ml 2.4M HCl. Subsequently, Pb was isolated from the matrix components. The latter is required to avoid isobaric overlap of the signals of ²⁰⁴Pb with ²⁰⁴Hg and the Oxides ¹⁹⁰Os¹⁶O, ¹⁹¹Ir¹⁶O, and ¹⁹²Os¹⁶O with ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb, respectively.

The sample solution (in 2.4M HCl medium) was loaded on the column. Matrix elements were eluted by 10 ml 2.4M HCl and discarded. Pb eluted by 3 ml 6M HCl. Each individual 1 ml fraction was analysed by quadrupole-based ICP-MS. Analyses demonstrated that about 90% of Pb was eluted within the second fraction of 6M HCl. The wall procedure was done without sample and used as blank.

Instrumentation

The instrument used for trace elements and isotope ratios measurements is a Perkin Elmer SCIEX ELAN6100 quadrupole-based ICP-mass spectrometer. A multi-channel peristaltic pump (Minipuls-3), a GemTip cross-flow nebuliser and a Perkin Elmer Type II spray chamber made of Rytan, drained by the peristaltic pump, were used for sample introduction. This instrument was further equipped with a Perkin Elmer corrosion-resistant torch with standard alumina injector and a Channeltron continuous dynode electron multiplier, operated in the pulse counting mode. Typical operation conditions have been summarized in Table 2. Measured masses were ⁸³Kr, ⁸⁴Sr, ⁸⁵Rb, ⁸⁶Sr, ⁸⁷Sr, ⁸⁸Sr, ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb and ²³⁸U. Automatic interference correction and blank subtraction were done using Elan-software.

RESULTS AND DISCUSSION

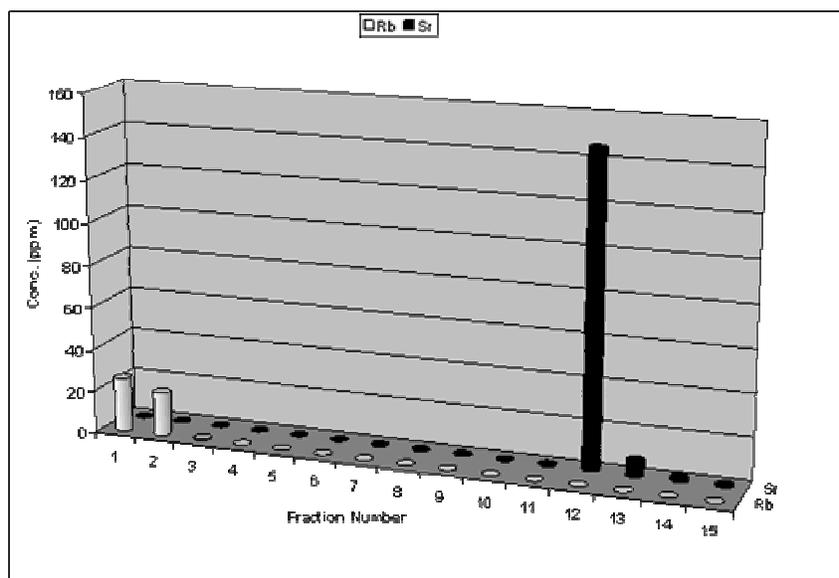
To fit an isochron from one bulk granite sample for age determination, physical separation of minerals is required. Table 3 shows granite forming minerals.

Trace elements concentrations in granite samples are shown in Table 4. Granite samples have been analyzed for minor and trace elements by ICP-MS. Granite samples SH and 143-a are characterized by high Na/K values and Al content, and can be considered as high Al A-type granitoids. Their molecular ratio Al₂O₃/(CaO+Na₂O+K₂O) are 1.06 and 1.16. Normative corundum ranges from 1.00 to 3.46 (Gomes and Neiva, 2005). Eby et al. (1992) divided the A-type granitoids into A1 and A2 chemical groups, based on tectonic affiliations and the Y/Nb ratios to differentiate between mantle (Y/Nb <1.2) and crustal (Y/Nb >1.2) origins. The studied A-type granitoids have Y/Nb ratios ranging from 1.38 to 8.01, and they are considered as A2 granitoids. This affiliation is consistent with the studied A-type granitoids' post-collisional or postorogenic environment and the derivation of the magma largely from arc-derived Pan-African mafic to intermediate continental crust (Faure, 1986).

Processing of ICP-MS ⁸⁷Sr/⁸⁶Sr and ²⁰⁶Pb/²⁰⁴Pb data: It is common knowledge that in ICP-MS, various phenome-

Table 1. Isobaric and polyatomic ions interfere with ^{86}Sr and ^{87}Sr .

Sr(86)		Sr(87)	
Interference species	Required resolution	Interference species	Required resolution
^{86}Kr	64074	^{87}Rb	296214
$^{38}\text{Ar}^{48}\text{Ti}$	61112	$^{36}\text{Ar}^{51}\text{V}$	33200
$^{36}\text{Ar}^{50}\text{Ti}$	19893	$^{40}\text{Ar}^{47}\text{Ti}$	16531
$^{36}\text{Ar}^{50}\text{Cr}$	15811	$^{71}\text{Ga}^{16}\text{O}$	8105
$^{38}\text{Ar}^{48}\text{Ti}$	14960	$^{69}\text{Ga}^{18}\text{O}$	5484
$^{40}\text{Ar}^{46}\text{Ti}$	14960	$^{174}\text{Yb}^{++}$	1436
$^{40}\text{Ar}^{46}\text{Ca}$	12625	$^{174}\text{Hf}^{++}$	1422
$^{70}\text{Ge}^{16}\text{O}$	8687		
$^{70}\text{Zn}^{16}\text{O}$	7835		
$^{68}\text{Zn}^{18}\text{O}$	5833		
$^{69}\text{Ga}^{17}\text{O}$	5566		
$^{173}\text{Yb}^{++}$	1459		

**Figure 1.** Strontium separation from matrix elements of granite using crown ether resin, where complete separation of strontium are obtained in a small volume (2 ml)

mena cause the relative ion intensities to vary as a function of the ion mass. These mass discrimination effects can occur during extraction (nozzle separation effect (Gillson et al., 1988)), transmission (space charge effects (Gillson et al., 1988; Tanner, 1992)) or detection, and they can amount to several per cent per mass unit. It is self-evident that for accurate isotope ratio determination and parent daughter ratio determination, mass discrimination has to be appropriately corrected for. In the case of Sr, this correction either (i) involves measurement of an (external) isotope ratio standard with a known isotopic composition or (ii) can be accomplished by monitoring $^{88}\text{Sr}/^{86}\text{Sr}$ isotope ratio for Sr measure-

ments and spiked $^{205}\text{Tl}/^{203}\text{Tl}$ isotope ratio for Pb measurements, which is constant in nature. Christensen et al. (1995) and Baker et al. (2004) In this work, external standardization was applied, using NIST SRM-987 (SrCO_3) and NIST SRM-981 (common lead) as an isotope ratio standards (NIST, Gaithersburg, MD, USA). On the basis of the results obtained from ICP-MS ($^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios & U and Pb contents isochrones to determine rocks formation age could be constructed. The content of ^{238}U can be calculated from the corresponding Pb elemental content. The content of ^{204}Pb , on the other hand, can be calculated from the Pb content as shown in the above section.

Table 2. Experimental conditions used in the measurements.

Instrument	ELAN6100 (Perkin Elmer-Sciex)
Nebulizer :	cross-flow type
Spray chamber:	Scott-type
Sample uptake/ mL.min ⁻¹ :	1.8
Wash solution:	1% HNO ₃
RF frequency/ MHz:	40.68
RF power/ W:	1150
Plasma gas flow rate:	15
Auxiliary gas flow rate:	1.0
Carrier gas flow rate:	0.95
Lens voltage:	adjusted daily
Detector:	26-segment dynode operating in both pulse and analogue modes
Instrument tuning:	Performed using a 10 µgL ⁻¹ solution of Be, Mg, Cu, Pb, and U
Data acquisition mode:	peak hopping
Number of scan weeps:	500
Dwell time per point:	50 ms
number of replicates:	10

Table 3. Mineralogical composition (wt %) of granite samples.

Minerals and chemical formula	Granite samples			
	SHA	98	143-a	SH
Muscovite 3T Si-rich K _{0.93} Na _{0.03} (Al _{1.54} FeO _{0.25} Mg _{0.21} Ti _{0.04})((Si _{3.34} Al _{0.066})O ₁₀)(OH) ₂	31.4	6.3	14.5	10.1
Albite, low Na(AlSi ₃ O ₈)	-	1.3	-	76.7
Quartz, low SiO ₂	17.7	31.2	9.5	13.2
Orthoclase sodian K _{0.58} Na _{0.42} AlSi ₃ O ₈	-	52	-	-
Biotite (K _{0.95} Na _{0.08} Ba _{0.97})(Mg _{4.88} Fe _{0.63} Al _{0.4} Ti _{0.09})(Al _{3.6} Si _{4.4} O ₂₀)F _{1.3}	-	9.2	-	-
Edenite NaCa ₂ Mg ₅ AlSi ₇ O ₂₂ (OH) ₂	13.4	-	11.4	-
Labradorite (Ca _{0.64} Na _{0.31})(Al _{1.775} Si _{2.275})O ₈	37.5	-	64.6	-

The isochron/errochron age was calculated using the regression analysis of York (1969). Errors are quoted at the 2-sigma level. The ⁸⁷Rb, ²³⁸U, ²³⁵U, and ²³²Th decay constants (Faure, 1986) used are 1.42x10⁻¹¹, 1.55x10⁻¹⁰, 9.85x10⁻¹⁰, and 4.95x10⁻¹¹ a⁻¹. The goodness of fit of the regression line is quoted as the MSWD (Mean Square of Weighted Deviates) of McIntyre et al. (1966). The cut-off point between isochron (MSWD <2.5) and errochron (MSWD >2.5) was made following the methods of Brooks et al. (1972).

Rb-Sr isotopic studies: Rb-Sr data for the SHA granite are given in Table (5). The Rb/Sr isotopic data for SHA

minerals yield an isochron age of 601±39 Ma and an initial ⁸⁷Sr/⁸⁶Sr ratio of 0.70012± 0.00717 (Figure 2). Rb-Sr age obtained by ICP-MS is in compatible with age obtained for rhyolite (572 Ma) from the same area (Shammar group) (Al-Shanty, 1993).

Rb-Sr data for the 98-whole rock and five mineral s separated from it define a 526±35 Ma isochron age with an initial ⁸⁷Sr/⁸⁶Sr ratio of 0.70462±0.00053 (Figure 2). Agreement is observed between granite sample 98 age and the age determined by thermal ionization mass spectrometry (VG Isomass 54E). Good agreement was observed between the age determined by ICP-MS and the age determined by TIMS for granite samples 143-a and SH,

Table 4. Minor and trace element concentrations (ppm) in granite samples.

Elements	Unit	SHA		98		143-a		SH	
		Conc.	RSD%	Conc.	RSD%	Conc.	RSD%	Conc.	RSD%
Na	%	2.33	2.30	3.41	0.63	3.45	2.82	3.53	1.13
Mg	%	0.62	1.33	0.34	2.23	1.66	3.03	0.81	1.38
Al	%	6.63	0.41	8.09	2.46	8.83	3.34	8.45	1.51
K	%	2.81	1.84	3.98	0.88	1.08	3.02	1.27	0.70
Ca	%	2.32	2.52	1.53	1.81	3.84	2.41	2.43	2.54
Fe	%	2.64	1.69	1.68	0.94	3.20	1.41	1.84	1.24
Mn	ppm	534	1.18	380	2.35	617	1.35	339	0.12
V	ppm	41.5	0.87	51	4.43	95.9	1.48	51.5	0.85
Li	ppm	19.1	1.96	54.1	1.89	16.5	1.14	25.2	1.08
Be	ppm	11.3	0.99	3.11	3.20	1.24	8.01	0.981	10.7
Co	ppm	12.3	1.40	16.3	1.36	19.3	1.39	34.5	1.41
Ni	ppm	13.2	0.72	22	2.38	22.8	0.23	11.2	0.7
Cu	ppm	13.3	1.19	13.9	1.51	8.33	3.38	15.5	1.12
Zn	ppm	279	1.18	59	1.05	85.2	1.11	62.6	1.19
Ga	ppm	41.5	1.91	21.7	0.73	19.5	0.81	17.7	2.07
Rb	ppm	193	0.96	163	0.17	27.5	2.39	33.6	1.3
Sr	ppm	96.6	1.36	387	1.63	852	1.06	405	2.04
Y	ppm	93.1	0.83	10.2	4.92	7.53	1.14	3.98	0.95
Mo	ppm	8.97	0.71	13	1.82	6.63	1.61	0.3	2.14
Nb	ppm	62.8	2.57	7.4	0.45	0.94	1.77	1.15	1.96
Ag	ppm	3.58	1.22	0.61	3.28	0.431	2.29	0.6	2.48
Cd	ppm	1.06	3.76	0.399	7.92	0.14	7.26	0.11	11.9
Ba	ppm	108	0.63	903	0.46	586	0.93	350	0.96
Tl	ppm	1.58	0.74	0.737	0.41	0.27	2.13	0.16	1.49
Pb	ppm	16.6	1.72	15.7	0.06	12.5	1.77	13.1	1.29
Bi	ppm	0.68	1.00	0.039	5.57	0.03	6.26	0.03	0.94
Th	ppm	9.18	2.04	47.18	4.15	19.11	2.22	15.91	3.88
U	ppm	6.14	0.46	1.58	0.61	0.785	1.30	0.46	1.3
Na/Al		0.35		0.42		0.39		0.42	
Na/K		0.83		0.86		3.19		2.78	
K/Rb		146		244		393		378	
Rb/Sr		1.998		0.421		0.032		0.083	
(Ga/Al)x10 ⁴		6.26		2.68		2.21		2.09	
Rb/Ba		1.787		0.181		0.047		0.096	
Y/Nb		1.48		1.38		8.01		3.46	
U/Pb		0.37		0.101		0.063		0.035	
□ ZrNbY		164.0		97.1		13.6		17.6	
$\frac{Al_2O_3}{(CaO + Na_2O + K_2O)}$		0.89		0.91		1.06		1.17	

as shown in Table 7, but with higher age deviation obtained by ICP-MS. The low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70012 ± 0.00717 , 0.70462 ± 0.00053 , 0.70417 ± 0.00017 , and 0.70388 ± 0.00057 obtained for SHA, 98, 143-a, and SH granite samples, respectively, are within the range (0.701-0.706) expected for rocks derived from mantle-like

protoliths (Al-Shanty, 1993), within the experimental error for SHA granite sample.

U-Pb isotopic studies

^{238}U - ^{206}Pb data for the granite samples are given in Ta-

Table 5. Experimentally determined $^{87}\text{Sr}/^{86}\text{Sr}$ by ICP-MS and calculated $^{87}\text{Rb}/^{86}\text{Sr}$ in granite samples (SHA, 98, 143-a, and SH).

Samples	Minerals	Rb (ppm)	Sr (ppm)	Rb/Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$
SHA	Whole rock	193±1.9	96.6±1.3	1.998	0.748067±0.001244	5.80324
	Edenite	140±3.3	114±1.1	1.228	0.728835±0.001975	3.55987
	Muscovite	177±1.3	107±1.4	1.654	0.739492±0.002234	4.80296
	Labradorite	194±2.5	87±0.5	2.230	0.753873±0.002279	6.48041
	Quartz	1.96±1.9	1.07±0.7	1.832	0.743903±0.001348	5.31745
98	Whole rock	163±0.3	387±6.3	0.421	0.714492±0.001112	1.21941
	Quartz	1.17±3.5	3.91±11.8	0.299	0.71127±0.002586	0.86605
	Biotite	325±6.4	278±3.8	1.169	0.730786±0.001302	3.39002
	Muscovite	389±4.4	275±4.8	1.415	0.73624±0.001299	4.10405
	Albite	368±10.4	302±7.3	1.219	0.731296±0.001643	3.53368
	Orthoclase	306±2.3	321±0.97	0.953	0.724524±0.001804	2.76258
143-a	Whole rock	27.5±0.7	852±9	0.032	0.705047±0.000931	0.09336
	Edenite	35±0.3	721±3.3	0.049	0.705913±0.001132	0.14042
	Muscovite	54±0.5	535±2.9	0.101	0.707280±0.001726	0.29202
	Labradorite	57±0.2	541±2.7	0.105	0.707560±0.000511	0.30483
	Quartz	0.38±0.6	8.41±5.4	0.045	0.705593±0.001777	0.13070
SH	Whole rock	33.6±0.4	405±8.3	0.083	0.706268±0.000976	0.23999
	Muscovite	28.6±0.1	484±0.9	0.058	0.706026±0.001099	0.16770
	Albite	20.2±0.4	473±7.2	0.042	0.705533±0.000940	0.12231
	Quartz	0.50±0.8	4.20±6	0.119	0.708035±0.001286	0.34907

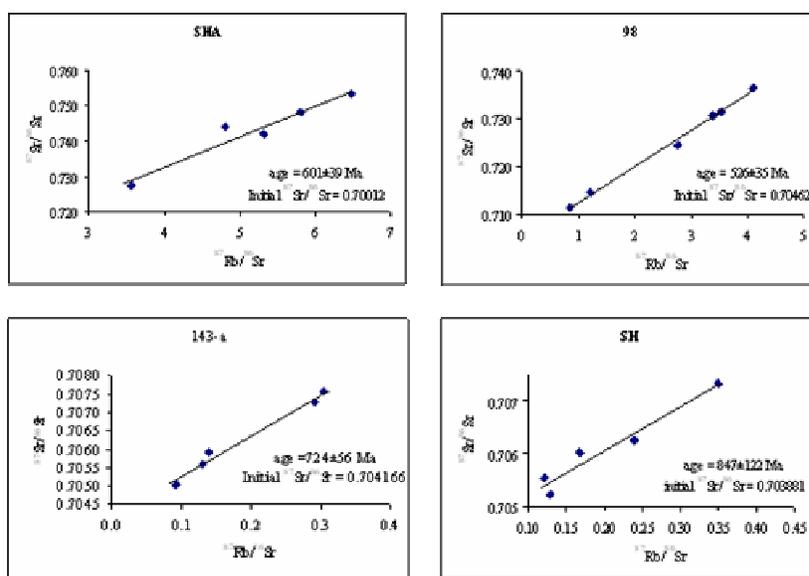
**Figure 2.** Rb/Sr isochron for granite samples (SHA, 98, 143-a, and SH), constructed based on the experimentally determined $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in separated minerals by magnetic separator.

Table 6. Experimentally determined $^{206}\text{Pb}/^{204}\text{Pb}$ by ICP-MS and calculated $^{238}\text{U}/^{204}\text{Pb}$ in granite samples.

Samples	Minerals	U	Pb	U/Pb	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{238}\text{U}/^{204}\text{Pb}$
SHA	Whole rock	6.14	16.6	0.3699	19.95221±0.08007	23.38546
	Edenite	8.66	28.8	0.3007	19.58041±0.05773	18.91706
	Muscovite	8.15	18.3	0.4455	20.38983±0.01275	28.31659
	Labradorite	5.91	13.7	0.4318	20.3644±0.07973	27.4498
	Quartz	8.04	19.3	0.4166	20.1856±0.01506	26.42033
98	Whole rock	15.7	1.58	9.94	19.06746±0.05878	6.295576
	Quartz	16.8	1.06	15.85	18.60028±0.09117	3.913457
	Edenite	16.7	2.47	6.76	19.36301±0.07457	9.279363
	Muscovite	16.5	3.41	4.84	19.40106±0.06332	13.19995
	Labradorite	17.8	5.75	3.09	20.26988±0.01203	21.03934
143-a	Whole rock	0.785	12.5	0.0628	17.42753±0.02319	3.83559
	Labradorite	0.75	7.69	0.0975	17.55517±0.03365	5.96743
	Quartz	0.965	8.87	0.1088	17.82819±0.09626	6.68217
SH	Whole rock	0.460	13.1	0.0351	17.99962±0.14037	2.16332
	Quartz	0.679	18.9	0.0359	17.98462±0.05756	2.21142
	Muscovite	0.453	8.89	0.051	18.20686±0.13349	3.14633
	Albite	0.831	9.22	0.0901	18.04707±0.05759	2.21176

Table 7. Final results for age determination of granite samples by ICP-MS compared with determined age using TIMS.

Samples	age (Ma) ICP-MS		Rb-Sr age (Ma) TIMS
	$^{238}\text{U} \rightarrow ^{206}\text{Pb}$	Rb-Sr	
SHA	536 ± 45	601 ± 39	572 ± 20 ⁽⁴⁵⁾
98	555 ± 43	526 ± 35	569 ± 12
SH	869 ± 85	847 ± 122	854 ± 10
143-a	746 ± 92	724 ± 55	726 ± 28

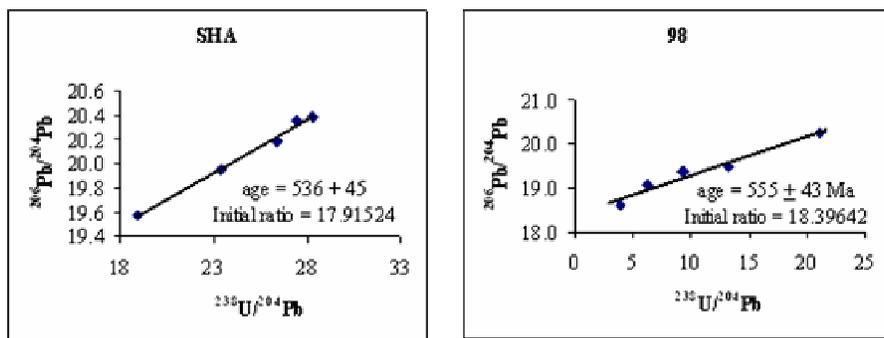


Figure 3. U/Pb isochrons for granite samples (SHA and 98), constructed based on the experimentally determined $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios in separated minerals by magnetic separator.

ble 6. The isotopic data for SHA minerals yield an isochron age of 536±45 Ma and an initial $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of

17.91524±0.12209 (Figure 3). U-Pb age obtained by ICP-MS is in agreement with Rb-Sr but lower than the

age obtained for rhyolite (572 Ma) from the same area (Faure, 1986). ^{238}U - ^{206}Pb isotopic data for granite sample 98 yield an isochron age of 555 ± 41 Ma. This age is in agreement with the age obtained by Rb-Sr method, and is slightly lower than the age obtained by TIMS. Good agreement is observed in age determined for granite sample SH and 143-a by ^{238}U - ^{206}Pb and Rb-Sr methods with the age obtained by TIMS, as shown in Table 7.

Conclusions

Although the isotope ratio precision obtained is clearly significantly poorer than that obtained with TIMS, the results for the granite rocks from the Arabian Shield demonstrate that relevant geochronological data can be derived from ICP-MS measurements. The case study clearly shows the merits of ICP-MS for exploratory studies of Sr and Pb isotope systematic and geochronology in cases where the expected variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are larger than the analytical precision. This means that single ion collector ICP-MS establishes a routine method of dating rocks for fast reconnaissance studies of areas where the geochronological history is unknown.

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