



## *In situ* U–Pb, Sr, Nd and Hf isotopic analysis of eudialyte by LA-(MC)-ICP-MS

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### ABSTRACT

Eudialytes are a group of complex Na–Ca zirconosilicate minerals that generally occur in peralkaline agpaitic syenites. Given that eudialytes are easily altered and commonly contain inclusions of earlier-crystallized minerals, *in situ* laser ablation is considered as the most suitable method to determine their U–Pb ages, and Sr, Nd and Hf isotopic compositions. Electron microprobe and LA-ICP-MS analysis of eudialytes from nepheline syenites from Ilímaussaq (Greenland), Khibiny and Lovozero (Russia), Saima (China), Tamazeght (Morocco), Kipawa and Mont Saint Hilaire (Canada), Poços de Caldas (Brazil) and Langesund Fjord (Norway), indicate that this mineral typically has high contents of U, Pb, Nb, Ta, Zr, Hf and rare earth elements (REE).

Analysis of an in-house standard eudialyte by both solution and laser ablation methods demonstrates that precise and accurate U–Pb ages can be obtained from eudialyte after correction for the common Pb content. The high Sr, Nd and Hf contents in eudialyte, coupled with the generally low Rb/Sr and Lu/Hf ratios, also permit the precise determination of *in situ* Sr, Nd and Hf isotopic ratios by LA-(MC)-ICP-MS methods. However, some eudialytes with Rb/Sr ratio of >0.02 and Yb/Sr>0.1, and Lu/Hf>0.08 (or Yb/Hf>0.4–0.5) cannot be used for *in situ* Sr and Hf isotopic measurement. Eudialyte is the only mineral investigated to date for which it is possible to determine simultaneously U–Pb ages and Sr, Nd and Hf isotopic compositions.

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### 1. Introduction

Sr, Nd and Hf isotopic data are essential for deciphering the petrogenesis of rocks. A common procedure utilized in the past was to obtain data by bulk rock elemental and isotopic analysis, and from these data determine the initial isotopic compositions. Problems with this approach are that samples are commonly contaminated by crustal and/or xenolithic material and thus the isotopic ratios determined do not represent those of the parental magma. To avoid such problems laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS), has been extensively used for *in situ* isotopic measurements as it can provide rapid, texturally sensitive, high precision isotopic data without the need for chemical preparation of the samples. For Sr isotopic analysis, *in situ* laser ablation techniques have been applied minerals with low Rb/Sr ratios, i.e., plagioclase, titanite, apatite and perovskite (Christensen et al., 1995; Ramos et al., 2004; Adams et al., 2005; Woodhead et al., 2005;

Davidson et al., 2007; Paton et al., 2007a,b; Yang et al., 2009). With regard to Nd, this technique has been recently applied to minerals with high Nd concentrations such as: apatite, titanite, monazite, allanite, and perovskite (Foster and Vance, 2006; McFarlane and McCulloch, 2007, 2008; Yang et al., 2008; Gregory et al., 2009; Wu et al., 2010; Yang et al., 2009). Hf isotopic analyses have been obtained for zircon, baddeleyite and rutile (Thirlwall and Walder, 1995; Griffin et al., 2000; Choukroun et al., 2005; Wu et al., 2006; Aulbach et al., 2008), as these minerals have high Hf concentrations and low Lu/Hf ratios.

Commonly, it is not possible to obtain Sr, Nd and Hf isotopic data from a single mineral phase. The ideal candidate has to have high Sr, Nd and Hf concentrations, coupled with low Rb/Sr and Lu/Hf ratios. Eudialyte group minerals have great potential for such multiple isotopic ratio determinations as recently shown by Kogarko et al. (2010).

On the basis of mineralogical differences and peralkalinity [molar (Na+K)/Al>1], igneous rocks are subdivided into miaskitic and agpaitic groups (Johnsen and Gault, 1997; Sørensen, 1997). In miaskitic rocks, zircon, baddeleyite, titanite, ilmenite and rutile are common; whereas in agpaitic rocks, complex Na–Ca zirconosilicates

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such as eudialyte, rinkite and l avenite are present (S orensen, 1997). This mineral assemblage is significantly different from that occurring in miassic rocks, in which zircon and titanite are characteristic minerals. Typically, eudialyte is found in peralkaline nepheline syenites such as the Khibiny and Lovozero complexes of the Kola Peninsula in Russia, the Ilmaussaq complex of South Greenland, the Tamazeght complex in Morocco, and the Pilanesberg complex in South Africa (Arzamastsev et al., 2005; Mitchell and Liferovich, 2006; Pfaff et al., 2008; Schilling et al., 2009). Rare examples of eudialyte-bearing granites are found at Ascension Island and Straumsvola in Antarctica (Olivo and Williams-Jones, 1999). Eudialyte group minerals may crystallize during the orthomagmatic as well as during late magmatic to hydrothermal stages (Kogarko et al., 1982; S orensen, 1997; Olivo and Williams-Jones, 1999; Mitchell and Liferovich, 2006; Schilling et al., 2009).

In this work, an analytical technique for the *in situ* determination of Sr, Nd and Hf isotopic ratios in eudialyte group minerals is presented. Our results, which generally compare very well with published solution data, demonstrate that direct *in situ* analysis of eudialyte for U–Pb ages, Sr, Nd and Hf isotopic compositions is generally possible and represents a powerful new method for evaluating the petrogenesis of apatitic magmatic systems.

## 2. Analytical methods

Eudialyte from nine localities was analysed for major and trace elements, U and Pb isotopic compositions, and Sr, Nd and Hf isotopic ratios. For an in-house standard, an eudialyte separate was obtained by crushing the rock sample, followed by handpicking the eudialyte crystals. These were embedded in epoxy and polished for subsequent *in situ* analyses. Some clean grains were selected for Sr, Nd and Hf isotopic analyses using isotope dilution (ID) methods in order to check the reliability and feasibility of the *in situ* analyses. All analyses were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences.

### 2.1. Major elements analyses

Major element compositions were obtained using a JEOL-JAX8100 electron microprobe with 15 kV accelerating potential and 12 nA beam current. Counting times were 20 s. Total iron is expressed as FeO. The analytical uncertainties are within 2% for SiO<sub>2</sub>, ZrO<sub>2</sub>, FeO, CaO and Na<sub>2</sub>O, but ~10–20% for other minor elements due to their low concentrations.

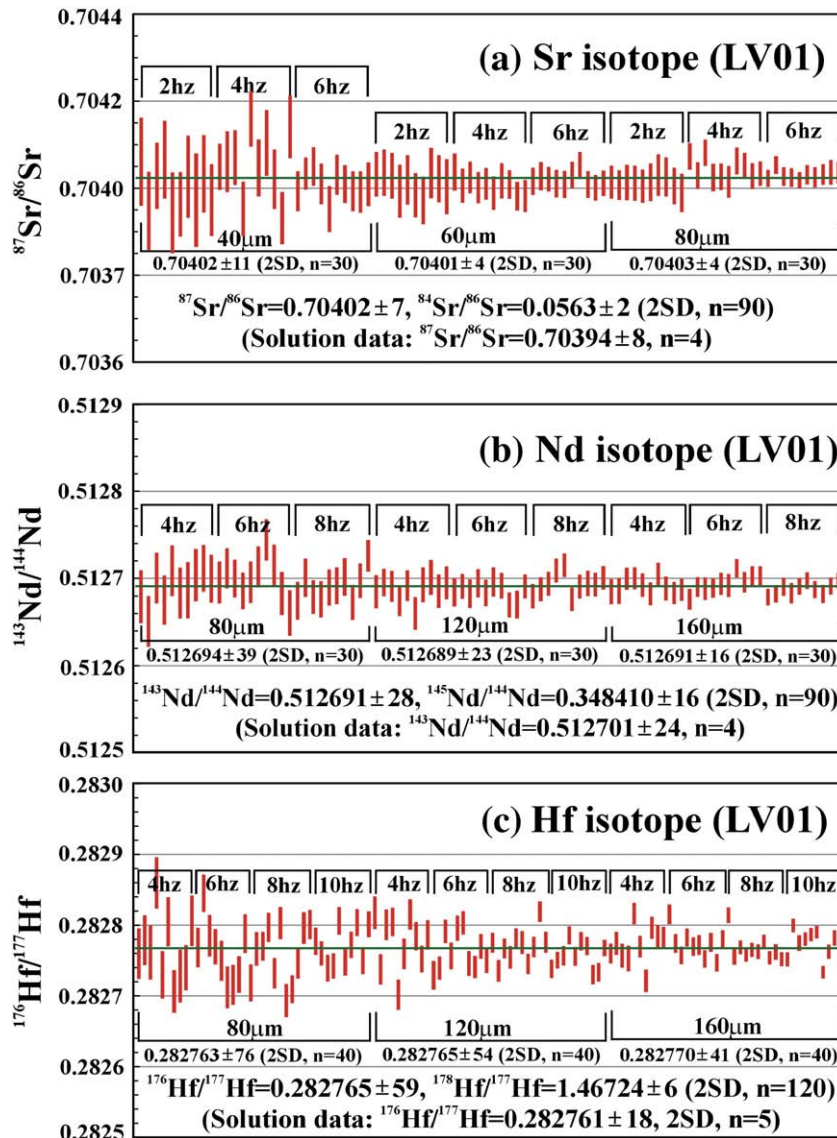


Fig. 1. *In situ* Sr–Nd–Hf isotopic analyses of in-house eudialyte standard of LV01.

**Table 1**

*In situ* Sr–Nd–Hf isotopic measurements (2SD) of in-house eudialyte standard (LV01) using different spot sizes and pulse rates.

<sup>87</sup> Sr/ <sup>86</sup> Sr ratio				
Solution data: <sup>87</sup> Rb/ <sup>86</sup> Sr = 0.0016, <sup>87</sup> Sr/ <sup>86</sup> Sr = 0.70394 ± 8 (2SD, n = 4)				
	40 μm	60 μm	80 μm	Average
2 Hz	0.704000 ± 93	0.704011 ± 46	0.704010 ± 23	0.704007 ± 60
4 Hz	0.704052 ± 146	0.704005 ± 36	0.704041 ± 46	0.704033 ± 97
6 Hz	0.704006 ± 55	0.704018 ± 30	0.704029 ± 20	0.704018 ± 41
Average	0.704020 ± 111	0.704011 ± 38	0.704027 ± 40	<b>0.704019 ± 72</b>
<sup>143</sup> Nd/ <sup>144</sup> Nd ratio				
Solution data: <sup>147</sup> Sm/ <sup>144</sup> Nd = 0.1173, <sup>143</sup> Nd/ <sup>144</sup> Nd = 0.512701 ± 24 (2SD, n = 4)				
	80 μm	120 μm	160 μm	Average
4 Hz	0.512690 ± 37	0.512687 ± 24	0.512691 ± 16	0.512689 ± 26
6 Hz	0.512700 ± 45	0.512685 ± 19	0.512694 ± 19	0.512693 ± 32
8 Hz	0.512691 ± 33	0.512694 ± 24	0.512688 ± 13	0.512691 ± 24
Average	0.512694 ± 39	0.512689 ± 23	0.512691 ± 16	<b>0.512691 ± 28</b>
<sup>176</sup> Hf/ <sup>177</sup> Hf ratio				
Solution data: <sup>176</sup> Lu/ <sup>177</sup> Hf = 0.00277, <sup>176</sup> Hf/ <sup>177</sup> Hf = 0.282761 ± 18 (2SD, n = 5)				
	80 μm	120 μm	160 μm	Average
4 Hz	0.282766 ± 92	0.282774 ± 75	0.282770 ± 52	0.282770 ± 73
6 Hz	0.282757 ± 85	0.282762 ± 53	0.282772 ± 38	0.282763 ± 61
8 Hz	0.282760 ± 79	0.282768 ± 46	0.282766 ± 37	0.282765 ± 55
10 Hz	0.282769 ± 53	0.282758 ± 37	0.282771 ± 42	0.282765 ± 45
Average	0.282763 ± 76	0.282765 ± 54	0.282770 ± 41	<b>0.282765 ± 59</b>

## 2.2. *In situ* trace elements and U–Pb analyses

Trace element compositions (including REE) and U–Pb age determinations were conducted using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS); the detailed analytical procedures are provided in Xie et al. (2008). The ArF excimer laser ablation system (Geolas CQ) is attached to an Agilent 7500a ICP-MS instrument. With a fluence of ~10 J/cm<sup>2</sup>, the selection of spot size (60–

160 μm) and repetition rate (3–10 Hz) depended on the signal intensity. During laser ablation, helium gas was flushed into the sample cell to minimize aerosol deposition around the ablation pit and argon gas was then used to improve transport efficiency. The background of <sup>204</sup>Pb and <sup>202</sup>Hg was less than 100 cps because of the use of high purity liquid argon and helium gas, compared to from <10 to 500 cps for eudialyte depending on its common Pb contents.

ICP-MS measurements were carried out using time-resolved analysis and peak hopping at one point per mass. Every five samples analysed were followed by one standard zircon 91500 and one NIST SRM 610 measurement. Each spot analysis consisted approximately of a 30 s background acquisition and 40 s sample data acquisition. <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>206</sup>Pb/<sup>238</sup>U, <sup>207</sup>U/<sup>235</sup>U (<sup>235</sup>U = <sup>238</sup>U/137.88) and <sup>208</sup>Pb/<sup>232</sup>Th ratios were corrected by using zircon 91500 as an external standard. The fractionation correction and results were calculated using GLITTER 4.0 (Griffin et al., 2008). All the measured isotope ratios of zircon 91500 during sample analysis were regressed and corrected using reference values. The relative standard deviations of reference values for zircon 91500 were set at 2%. After obtaining the Pb isotopic ratios, the <sup>207</sup>Pb method was applied for common Pb corrections using the upper intercept obtained from a Tera–Wasserburg diagram. Subsequently, <sup>206</sup>Pb/<sup>238</sup>U weighted ages were calculated using ISOPLOT 3.0 (Ludwig, 2003). Errors of individual analyses are based on counting statistics and are given at the 1σ level, although errors on pooled ages are quoted at the 2σ or 95% confidence level. Trace element concentrations were calculated using GLITTER 4.0 and calibrated using <sup>40</sup>Ca as an internal standard and NIST610 as an external reference material. The analytical uncertainties are mostly within 10%.

## 2.3. Sr–Nd–Hf analyses by isotope dilution

Chemical separation was undertaken by conventional ion-exchange techniques. The detailed procedure is discussed by Yang et al. (2010), and only a brief introduction is given here. Eudialyte crystals were dissolved with a mixed spike (<sup>87</sup>Rb–<sup>84</sup>Sr, <sup>149</sup>Sm–<sup>150</sup>Nd and <sup>176</sup>Lu–<sup>180</sup>Hf) in 2.5 ml concentrated HF, 0.2 ml HNO<sub>3</sub> and HClO<sub>4</sub> using

**Table 2**

Chemical compositions of studied eudialyte, titanite and apatite.

Sample	GM1370	GM1369	KP21	KP58	GM1335	ILM101	KB-0	KB-0 Ap	KB-0 Tit	KB-1	KB-1 Ap	KB-1 Tit	KB-2	KB-3	KB-3 Ap	LV-13
<i>Major elements (wt.%)</i>																
SiO <sub>2</sub>	53.64	53.29	54.19	54.94	52.45	52.91	51.50	0.11	32.36	51.29	0.28	31.43	51.31	52.06	0.18	50.61
TiO <sub>2</sub>	0.03	0.02	0.01	0.01	0.01	0.01	0.36	0.01	38.16	0.57	0.01	37.60	0.84	0.31	0.01	0.78
ZrO <sub>2</sub>	12.63	12.56	12.85	12.97	12.45	12.66	12.64	1.19	0.18	12.98	1.21	0.22	12.45	11.64	1.22	14.39
Nb <sub>2</sub> O <sub>5</sub>	0.54	0.15	0.54	0.32	0.48	0.35	0.08	0.17	1.24	0.08	0.13	0.35	0.12	0.00	0.03	0.29
La <sub>2</sub> O <sub>3</sub>	0.41	0.42	0.63	1.01	0.46	0.47	0.03	0.19	0.04	0.03	0.37	0.07	0.04	0.05	0.37	0.24
Ce <sub>2</sub> O <sub>3</sub>	0.84	0.93	1.51	2.22	0.95	0.87	0.11	0.25	0.09	0.08	0.65	0.24	0.13	0.11	0.62	0.63
Pr <sub>2</sub> O <sub>3</sub>	0.12	0.09	0.15	0.25	0.14	0.09	0.04	0.05	0.06	0.05	0.09	0.06	0.03	0.05	0.06	0.07
Nd <sub>2</sub> O <sub>3</sub>	0.33	0.27	0.61	0.94	0.29	0.24	0.00	0.05	0.04	0.00	0.18	0.06	0.00	0.01	0.18	0.02
MgO	0.02	0.02	0.00	0.01	0.02	0.02	0.03	0.01	0.00	0.03	0.01	0.03	0.02	0.07	0.01	0.06
FeO	4.60	4.44	5.13	2.62	6.58	6.46	6.04	0.02	0.72	5.27	0.00	1.12	5.74	6.22	0.02	3.02
MnO	0.84	1.06	1.38	1.77	0.60	0.97	0.74	0.01	0.04	0.35	0.01	0.04	0.55	0.39	0.01	2.77
CaO	10.99	10.81	9.94	8.22	11.11	10.54	12.14	54.41	27.48	11.51	50.21	27.80	11.59	12.12	51.46	7.85
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.09	2.61	0.03	0.31	7.20	0.13	0.02	0.04	4.51	0.62
Na <sub>2</sub> O	12.11	13.53	11.88	12.84	12.22	13.51	14.53	0.10	1.11	14.46	0.18	0.49	14.84	14.10	0.19	17.68
Cl	1.03	1.25	0.46	0.45	1.08	0.94	1.27	0.00	0.00	1.25	0.00	0.01	1.27	0.88	0.00	1.15
Total	98.14	98.84	99.29	98.56	98.82	100.03	99.59	100.80	101.63	98.27	100.31	99.72	98.94	98.04	97.61	100.18
<i>Trace elements (ppm)</i>																
U	67	32	140	253	40	46	44	1.9	4.6	27	1.4	1.7	69	30	1.3	31
Th	35	16	68	79	23	21	18	21	12	15	16	7.8	34	14	20	44
Pb	107	84	1212	80	83	136	24	1.9	1.5	14	1.1	0.76	16	15	1.2	41
Rb	26	9.4	101	31	8.6	37	5.9	0.15	7.8	25	2.0	8.7	4.7	24	0.18	9.8
Sr	147	814	1047	1016	655	649	6575	25895	2138	10579	83976	5403	7642	9132	45663	17928
Sm	913	797	1768	2054	741	772	77	134	98	106	238	172	123	80	259	881
Nd	3770	3676	9262	10901	3560	3602	235	939	467	391	1988	1014	486	287	1937	3218
Lu	181	92	135	128	102	101	22	0.73	0.8	20	0.71	1.0	18	18	0.85	77
Yb	1123	616	957	918	639	638	144	8.1	11	130	8.1	13	131	122	10	498
Hf	2176	2134	1944	1600	2201	2117	1403	0.03	36	1614	0.16	75	1221	1646	0.02	2251

steel-jacketed Teflon bombs placed in an oven for a week at 190 °C. Following complete dissolution and spike-sample homogenization, each sample was dried down at high temperature (fuming HClO<sub>4</sub>) on a hot plate; then the mixture was treated with 6 M HCl, evaporated to dryness, and taken up in 3 M HCl before chemical separation. The treatment with 6 M HCl is necessary to completely convert fluorides into chlorides (Münker et al., 2001).

The first stage was the separation of Lu and Hf from the matrix using Eichrom Ln-spec resin (100–150 μm, 2 ml), modified from the procedure of Münker et al. (2001). The major element and light and middle rare earth element (L(M)REE) fraction was eluted and collected using 3 M HCl and 4 M HCl for further purification. After collecting the Lu (+ Yb) fraction using 4 M HCl, the column was rinsed with 6 M HCl to remove effectively any remaining Lu and Yb before collection of the Hf fraction, followed by separation of Ti from Hf using an HCl + H<sub>2</sub>O<sub>2</sub> mixture. In addition, the Hf fraction was eluted with 2 M HF. The second stage involved standard cation exchange chromatography for Rb and Sr purification. The L(M)REE eluted with 6 M HCl were further purified using another Eichrom Ln resin (100–150 μm, 2 ml) with 0.25 M HCl for Nd and 0.40 M HCl for Sm, modified from the technique of Pin and Zalduegui (1997). In order to check the reliability of procedure, apatite and titanite from the same rocks were also selected for Sr and Nd isotopic analyses. The chemical separation procedure was similar to that described above except that separation of Lu and Hf was not attempted.

Rb, Sr, Sm and Nd concentrations and Sr–Nd isotopes were analysed using a Finnigan MAT 262 thermal ionization mass spectrometer (TIMS). Procedural blanks were less than 100 pg for Rb and Sr, and 50 pg for Sm and Nd. <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd ratios were normalized to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194 and <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219 using the exponential law. Isotopic analyses of Lu and Hf were collected using a Neptune MC-ICP-MS and followed the methods of Vervoort et al. (2004). Typical analytical blanks were less than 50 pg for Hf and 10 pg for Lu. Hafnium isotope ratios were corrected for instrumental mass bias to <sup>179</sup>Hf/<sup>177</sup>Hf = 0.7325 using the exponential law. During the period of data acquisition, standard analyses yielded

results of <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710250 ± 11 (2SD, n = 18) for NBS987, <sup>143</sup>Nd/<sup>144</sup>Nd = 0.512120 ± 12 (2SD, n = 12) for JNdi-1, and <sup>176</sup>Hf/<sup>177</sup>Hf = 0.282165 ± 10 (2SD, n = 10) for JMC475. In addition, USGS reference materials BCR-1 and BHVO-2 were also processed for Sr–Nd–Hf isotopes, and gave ratios of 0.704977 ± 12 and 0.703474 ± 11 for <sup>87</sup>Sr/<sup>86</sup>Sr, 0.512655 ± 5 and 0.513000 ± 15 for <sup>143</sup>Nd/<sup>144</sup>Nd and 0.282866 ± 6 and 0.283109 ± 5 for <sup>176</sup>Hf/<sup>177</sup>Hf, respectively, which is identical, within error, to the recommended values (Weis et al., 2005, 2006, 2007).

#### 2.4. In situ Sr–Nd–Hf isotopic analyses by laser ablation

The *in situ* Sr–Nd–Hf isotopic analyses were conducted using the Neptune MC-ICP-MS machine. Detailed analytical protocols were given by Yang et al. (2007, 2009) and Wu et al. (2006), only a brief review is given here.

The *in situ* Sr isotopic data were acquired in static, multi-collector mode with low resolution using nine Faraday collectors, and the mass configuration array from <sup>83</sup>Kr to <sup>88</sup>Sr. During analyses, a 50 s measurement of the gas blank was carried out prior to ablation in order to correct for Kr assuming <sup>83</sup>Kr/<sup>84</sup>Kr = 0.20175 and <sup>83</sup>Kr/<sup>86</sup>Kr = 0.66474. The natural ratio of <sup>85</sup>Rb/<sup>87</sup>Rb of 2.5926 was used for isobaric correction of Rb by the exponential law, assuming that rubidium has the same mass discrimination as strontium (Ehrlich et al., 2001). No correction was applied for the interference of Ca argide/dimer species as our experiments demonstrated that this interference is negligible (e. g., Ehrlich et al., 2001; Fortunato et al., 2004; Ramos et al., 2004; Vroon et al., 2008). Interferences from Fe dioxides, and Ga and Zn oxides, are not considered in this study, due to their low signals during actual analyses. However, interference from the doubly charged rare earth elements (REEs) is not negligible when eudialyte was ablated for Sr and Nd isotopic measurements, due to the high concentrations of REEs. Based on the method proposed by Ramos et al. (2004), we monitored the presence of <sup>167</sup>Er<sup>2+</sup>, <sup>171</sup>Yb<sup>2+</sup> and <sup>173</sup>Yb<sup>2+</sup> at masses 83.5, 85.5 and 86.5. Then the contributions of <sup>168</sup>Er<sup>2+</sup> and <sup>168</sup>Yb<sup>2+</sup> to <sup>84</sup>Sr, <sup>170</sup>Er<sup>2+</sup> and <sup>170</sup>Yb<sup>2+</sup> to <sup>85</sup>Sr (+<sup>85</sup>Rb), <sup>172</sup>Yb<sup>2+</sup> to <sup>86</sup>Sr, <sup>174</sup>Yb<sup>2+</sup> to <sup>87</sup>Sr

LV01	LV02	LV03	LV04	SM6	SM06 Tit	SM7	SM25	TMZ177	TMZ241	TMZ298	MSH38	MSH52	PDC	KPW	LGS	LGS Ap
54.41	52.62	53.14	52.87	52.96	31.93	53.76	57.38	54.56	51.94	51.82	49.33	48.80	55.00	52.91	50.30	0.45
0.55	0.44	0.45	0.44	0.28	37.80	0.31	0.24	0.28	0.22	0.30	0.13	0.01	0.54	0.30	0.09	0.00
12.47	12.34	12.42	11.95	11.92	0.26	11.94	13.22	13.59	12.19	12.17	11.58	11.71	12.02	11.79	11.82	1.22
0.08	0.17	0.03	0.05	0.13	0.28	0.17	0.25	0.67	0.18	0.64	1.48	2.09	0.57	0.21	1.22	0.10
0.39	0.33	0.31	0.30	0.20	0.14	0.12	0.56	0.49	0.32	0.10	1.04	0.88	0.22	0.28	0.80	0.52
0.71	0.71	0.70	0.68	0.35	0.53	0.27	1.20	0.51	0.36	0.12	1.85	1.41	0.26	0.54	0.93	1.14
0.07	0.11	0.04	0.13	0.06	0.07	0.08	0.15	0.08	0.03	0.04	0.16	0.11	0.06	0.08	0.09	0.11
0.09	0.14	0.11	0.13	0.06	0.22	0.03	0.26	0.00	0.00	0.00	0.08	0.05	0.00	0.15	0.03	0.40
0.06	0.09	0.06	0.08	0.07	0.01	0.06	0.04	0.01	0.03	0.02	0.05	0.01	0.05	0.08	0.04	0.01
3.24	4.93	4.77	5.00	6.57	0.99	6.88	4.08	4.16	5.14	5.62	4.58	6.22	3.39	2.35	6.25	0.02
2.56	2.06	2.14	1.97	1.02	0.04	0.85	2.28	4.07	2.75	1.86	4.88	3.05	3.81	1.31	2.65	0.03
10.41	10.08	10.18	10.15	10.90	26.56	11.09	7.85	10.38	10.53	13.40	8.82	10.27	11.03	12.77	11.83	56.01
0.41	0.09	0.17	0.31	1.79	0.51	1.91	1.60	0.29	0.78	1.66	0.28	0.00	1.59	0.00	0.00	0.14
14.30	15.13	14.59	15.17	12.64	0.86	12.85	8.06	10.20	14.09	11.57	13.14	14.01	10.89	12.79	11.71	0.27
0.71	0.74	0.75	0.69	0.95	0.01	0.86	0.62	0.18	0.65	0.64	0.42	1.00	0.88	0.55	0.67	0.01
100.45	99.97	99.86	99.92	99.89	100.29	101.19	97.80	99.46	99.21	99.96	97.82	99.63	100.30	96.11	98.42	101.40
66	34	38	41	77	39	388	475	346	69	41	82	42	40	53	23	18
66	23	24	23	64	46	650	264	173	35	19	129	36	26	26	204	161
30	35	32	31	146	13	105	68	242	163	95	207	109	40	112	472	10
7.8	7.8	8.8	8.7	6.4	1.0	6.9	12	28	17	16	13	15	34	45	15	0.31
13606	10289	11491	10731	27323	9219	25352	22514	15250	14132	25699	10796	108	21913	1405	2409	1518
678	503	532	523	292	360	279	874	78	58	19	714	530	45	858	188	547
3887	2815	3068	2879	1261	2101	1081	4260	843	482	169	4918	3253	331	2526	1479	4107
58	44	43	43	44	0.54	52	38	13	28	11	60	130	14	577	71	6.8
392	293	292	288	257	7.4	302	248	77	151	63	423	750	78	4577	445	59
2986	2321	2451	2432	2510	134	2314	2235	1165	1149	1355	1561	1903	1924	2029	4226	0.17

(+<sup>87</sup>Rb), and <sup>176</sup>Yb<sup>2+</sup> to <sup>88</sup>Sr were calculated according to the isotopic abundances of Er and Yb (Chartier et al., 1999; Vervoort et al., 2004). However, no corrections of <sup>176</sup>Lu<sup>2+</sup> and <sup>176</sup>Hf<sup>2+</sup> on <sup>88</sup>Sr were made in this study since their signal intensities are low. During our data reduction, the effects of interfering elements were accounted for in the order of Kr, Yb<sup>2+</sup>, Er<sup>2+</sup> and Rb. In order to avoid the potential matrix-matched effect during laser ablation, an in-house eudialyte standard (LV01) was used for external correction during analyses.

The laser ablation Nd isotope technique is similar to that for Sr isotope analysis described above. Before analysis, a standard Nd solution was used to calibrate the machine using the exponential law for mass bias correction and assuming <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219. For *in situ* Nd isotopic analyses, the interferences are principally caused by Ce (<sup>142</sup>Ce on <sup>142</sup>Nd) and Sm (<sup>144</sup>Sm on <sup>144</sup>Nd). Our previous work indicated that the influence of Ce on Nd isotope analysis is insignificant when the Ce/Nd ratio is ≤ 3, which is the normal value in natural geological materials (Yang et al., 2007). For the interference of <sup>144</sup>Sm on <sup>144</sup>Nd, the mass bias of Sm ( $\beta_{Sm}$ ) was directly obtained from the <sup>147</sup>Sm/<sup>149</sup>Sm ratio on the sample itself and then applied in the isobaric interference correction, following the method proposed by McFarlane and McCulloch (2007), but with constant values of <sup>147</sup>Sm/<sup>149</sup>Sm = 1.08680 and <sup>144</sup>Sm/<sup>149</sup>Sm = 0.22332 (Yang et al., 2008). In addition, the stable <sup>145</sup>Nd/<sup>144</sup>Nd ratio of 0.348415 was used to evaluate the feasibility of our method. In order to evaluate measurement and potential matrix-matched effects, in-house standard of eudialyte (LV01) was used for external correction.

During Hf isotopic analyses, the isobaric interference of <sup>176</sup>Lu on <sup>176</sup>Hf is minor due to the low <sup>176</sup>Lu/<sup>177</sup>Hf in eudialyte (normally <0.01, which corresponds to a Lu/Hf ratio of ~0.07). In this study, <sup>176</sup>Lu/<sup>177</sup>Lu = 0.02655 was used to extract the interference of <sup>176</sup>Lu to <sup>176</sup>Hf. However, the interference of <sup>176</sup>Yb on <sup>176</sup>Hf must be carefully corrected since the contribution of <sup>176</sup>Yb to <sup>176</sup>Hf could profoundly

affect the accuracy of the measured <sup>176</sup>Hf/<sup>177</sup>Hf ratio. We used the mean <sup>173</sup>Yb/<sup>172</sup>Yb ratio of the individual spots to calculate the fractionation coefficient ( $\beta_{Yb}$ ) and the contribution of <sup>176</sup>Yb to <sup>176</sup>Hf (Wu et al., 2006) by applying ratios of <sup>176</sup>Yb/<sup>172</sup>Yb = 0.5887 and <sup>173</sup>Yb/<sup>172</sup>Yb = 0.73925. Zircon standard of 91500 and an in-house eudialyte standard of LV01 were used for external correction. During analytical sessions, the obtained <sup>176</sup>Hf/<sup>177</sup>Hf value for 91500 was 0.282301 ± 3 (2 $\sigma$ ,  $n = 114$ ) or 0.282303 ± 28 (2SD), which is similar to the values obtained by the solution method within error (Wiedenbeck et al., 1995; Woodhead et al., 2004; Wu et al., 2006; Blichert-Toft, 2008). For the in-house eudialyte standard, the details are described below.

### 3. Sr–Nd–Hf isotopic analyses of the in-house standard

Currently, there is no eudialyte isotopic standard. To check the reliability of our methods, an in-house eudialyte standard (termed LV01) was analysed by solution and laser ablation methods. This standard eudialyte, with a grain-size of ~10 × 8 × 6 mm<sup>3</sup>, originates from a pegmatitic syenite occurring in the Lovozero alkaline complex (Kola, Russia).

The Sr isotopic analysis was carried out with spot sizes of 40, 60 and 80 μm and repetition pulse rates of 2, 4 and 6 Hz. Each ten measurements were collected and the average <sup>87</sup>Sr/<sup>86</sup>Sr ratios, with 2SD are reported (Fig. 1a, Table 1). As can be seen in Table 1, signal intensity increases with spot size, resulting in a higher precision for a larger spot size. There is no correlation between the pulse rate and data precision (Fig. 1a) and the obtained <sup>87</sup>Sr/<sup>86</sup>Sr ratios for three different spot sizes are identical within error, with an average value of 0.70402 ± 7 (2SD,  $n = 90$ ) (Fig. 1a). The average <sup>84</sup>Sr/<sup>86</sup>Sr ratio of 0.0563 ± 2 (2SD,  $n = 90$ ) is identical to the theoretical value of 0.0565 within error. Using the solution method, LV01 has an <sup>87</sup>Sr/<sup>86</sup>Sr ratio of

**Table 3**  
*In situ* laser ablation Sr–Nd–Hf isotopic data of eudialyte, titanite and apatite.

Sample	Location	Mineral	U–Pb age	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr	2 $\sigma$	$I_{Sr}$	<sup>147</sup> Sm/ <sup>144</sup> Nd	<sup>143</sup> Nd/ <sup>144</sup> Nd	2 $\sigma$	$\epsilon_{Nd}(t)$	2 $\sigma$	<sup>176</sup> Lu/ <sup>177</sup> Hf	<sup>176</sup> Hf/ <sup>177</sup> Hf	2 $\sigma$	$\epsilon_{Hf}(t)$	2 $\sigma$
GM1370	Ilmaussaq	Eudialyte	1041 ± 17					0.1462	0.512193	12	−1.18	0.23	0.00842	0.282337	15	3.81	0.53
GM1369	Ilmaussaq	Eudialyte	1108 ± 21	0.01860	0.70853	3	0.7082	0.1346	0.512083	10	−1.61	0.20	0.00467	0.282232	9	3.00	0.32
KP21	Ilmaussaq	Eudialyte	1018 ± 34					0.1396	0.512067	21	−2.66	0.41					
KP58	Ilmaussaq	Eudialyte	1102 ± 12					0.1327	0.512049	9	−1.99	0.18					
GM1335	Ilmaussaq	Eudialyte	1118 ± 28					0.1288	0.512044	12	−1.50	0.23	0.00496	0.282239	9	3.02	0.32
ILM101	Ilmaussaq	Eudialyte	1134 ± 29					0.1325	0.512059	11	−1.76	0.21	0.00512	0.282250	13	3.29	0.46
KB-0	Khibiny	Eudialyte	368 ± 7	0.00261	0.70350	2	0.7035	0.2044	0.512933	6	5.40	0.12	0.00164	0.282804	10	8.88	0.35
KB-0 (Tit)	Khibiny	Titanite	369 ± 10	0.00015	0.70339	2	0.7034	0.1362	0.512720	13	4.46	0.25					
KB-0 (Ap)	Khibiny	Apatite	361 ± 15	0.00001	0.70343	2	0.7034	0.0932	0.512611	18	4.37	0.35					
KB-1	Khibiny	Eudialyte	365 ± 8	0.00764	0.70346	1	0.7035	0.1653	0.512853	11	5.68	0.21	0.00140	0.282797	9	8.69	0.32
KB-1 (Tit)	Khibiny	Titanite	351 ± 17	0.00007	0.70318	2	0.7032	0.1101	0.512689	7	5.09	0.14					
KB-1 (Ap)	Khibiny	Apatite	357 ± 16	0.00004	0.70327	2	0.7033	0.0775	0.512579	9	4.49	0.18					
KB-2	Khibiny	Eudialyte	358 ± 9	0.00156	0.70339	1	0.7034	0.1648	0.512826	6	5.18	0.12	0.00203	0.282805	7	8.82	0.25
KB-3	Khibiny	Eudialyte	362 ± 9	0.00368	0.70343	2	0.7034	0.1861	0.512868	10	4.99	0.20	0.00149	0.282806	9	8.98	0.32
KB-3 (Ap)	Khibiny	Apatite	355 ± 21	0.00001	0.70325	2	0.7032	0.0852	0.512592	9	4.38	0.18					
KB-3 (Ap)	Khibiny	Apatite						0.0860	0.512609	4	4.67	0.08					
LV13	Lovozero	Eudialyte	371 ± 29	0.00208	0.70378	1	0.7038	0.1641	0.512739	6	3.51	0.12	0.00363	0.282741	9	6.16	0.32
LV01	Lovozero	Eudialyte	376 ± 6	0.00247	0.70395	1	0.7039	0.1240	0.512672	5	4.10	0.10	0.00254	0.282788	12	8.09	0.42
LV02	Lovozero	Eudialyte	359 ± 8	0.00353	0.70400	2	0.7040	0.1221	0.512662	8	4.00	0.16	0.00260	0.282775	10	7.61	0.35
LV03	Lovozero	Eudialyte	361 ± 15	0.00306	0.70404	1	0.7040	0.1212	0.512665	7	4.10	0.14	0.00267	0.282789	5	8.09	0.18
LV04	Lovozero	Eudialyte	373 ± 7	0.00286	0.70403	2	0.7040	0.1239	0.512666	7	3.99	0.14	0.00262	0.282790	13	8.14	0.46
SM06	Saima	Eudialyte	209 ± 14	0.00079	0.70855	2	0.7086	0.1422	0.511929	8	−12.27	0.16	0.00203	0.282318	8	−11.42	0.28
SM06(Tit)	Saima	Titanite	224 ± 5	0.00005	0.70833	3	0.7083	0.1211	0.511872	13	−12.78	0.25					
SM07	Saima	Eudialyte	224 ± 4	0.00085	0.70854	1	0.7085	0.1537	0.511928	6	−12.62	0.12	0.00149	0.282335	13	−10.74	0.46
SM25	Saima	Eudialyte	193 ± 3	0.00158	0.70857	2	0.7086	0.1329	0.511896	10	−12.65	0.20	0.00198	0.282348	10	−10.35	0.35
TMZ 177	Tamazeght	Eudialyte	40 ± 5	0.00668	0.70324	2	0.7032	0.0588	0.512814	7	4.21	0.14	0.00143	0.282912	9	5.87	0.32
TMZ 241	Tamazeght	Eudialyte	43 ± 35	0.00420	0.70336	2	0.7034	0.0742	0.512807	7	3.98	0.14	0.00251	0.282875	6	4.53	0.21
TMZ 298	Tamazeght	Eudialyte	43 ± 24	0.00236	0.70320	2	0.7032	0.0741	0.512837	14	4.57	0.27	0.00110	0.282905	8	5.64	0.28
MSH 38	Mt–St Hilaire	Eudialyte	128 ± 12	0.00580	0.70385	3	0.7038	0.1107	0.512789	8	4.37	0.16	0.00548	0.283033	14	11.62	0.50
MSH 52	Mt–St Hilaire	Eudialyte	137 ± 17					0.0980	0.512811	6	5.01	0.12	0.00788	0.282949	14	8.44	0.50
PDC	Poços de Caldas	Eudialyte	77 ± 13	0.00457	0.70529	2	0.7053	0.0851	0.512413	10	−3.25	0.20	0.00077	0.282653	11	−2.49	0.39
KPW	Kipawa	Eudialyte	1012 ± 16					0.2438	0.512403	6	−10.64	0.12					
LGS	Langesundsfjord	Eudialyte						0.0847	0.512610	6	3.17	0.12	0.00246	0.282833	7	7.45	0.25
LGS	Langesundsfjord	Apatite	260 ± 4	0.00029	0.70366	2	0.7037	0.0913	0.512667	18	4.07	0.35					

**Table 4**  
Solution Sr–Nd–Hf isotopic data of eudialyte, titanite and apatite.

Sample	Mineral	Rb	Sr	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr	2σ	I <sub>Sr</sub>	Sm	Nd	<sup>147</sup> Sm/ <sup>144</sup> Nd	<sup>143</sup> Nd/ <sup>144</sup> Nd	2σ	ε <sub>Nd</sub> (t)	2σ	Lu	Hf	<sup>176</sup> Lu/ <sup>177</sup> Hf	<sup>176</sup> Hf/ <sup>177</sup> Hf	2σ	ε <sub>Hf</sub> (t)	2σ	
GM1370	Eud	54	134	1.1607	0.732185	26	0.7129	737	3012	0.1478	0.512164	7	−1.99	0.13	84.8	1352	0.0089	0.282318	5	2.75	0.18	
GM1370	Eud-R	57	143	1.1675	0.730879	31	0.7115	748	3216	0.1407	0.512145	6	−1.30	0.12								
KP21	Eud	134	852	0.4557	0.728132	36	0.7206	1380	6521	0.1279	0.512087	7	−0.53	0.15	91.8	1305	0.0100	0.282416	6	5.38	0.20	
KP58	Eud							1880	8981	0.1266	0.512070	13	−0.66	0.25	89.0	961	0.0132	0.282360	4	0.97	0.13	
KB-0	Eud-1	6.5	6680	0.0028	0.703511	16	0.7035	71	222	0.1930	0.512949	7	6.25	0.14	16.1	1150	0.0020	0.282815	4	9.16	0.14	
KB-0	Eud-1R1														19.3	1138	0.0024	0.282809	4	8.86	0.14	
KB-0	Eud-1R2														18.6	1140	0.0023	0.282811	4	8.97	0.14	
KB-0	Eud-2	6.4	6498	0.0028	0.703430	12	0.7034	69	218	0.1919	0.512896	16	5.27	0.31	13.2	931	0.0020	0.282813	6	9.09	0.21	
KB-0	Eud-2R1														18.4	917	0.0028	0.282808	7	8.70	0.25	
KB-0	Eud-2R2														17.0	922	0.0026	0.282797	7	8.39	0.25	
KB-0	Eud-3	6.5	6477	0.0029	0.703460	16	0.7034	69	217	0.1914	0.512933	6	6.01	0.11	15.2	963	0.0022	0.282811	5	8.97	0.18	
KB-0	Eud-3R														16.5	955	0.0025	0.282809	4	8.86	0.13	
KB-0	Tit	1.17	2307	0.0015	0.703373	9	0.7034	99	479	0.1251	0.512712	11	4.84	0.21								
KB-0	Ap	0.46	38128	0.0000	0.703415	13	0.7034	118	847	0.0845	0.512648	10	5.51	0.20								
KB-1	Eude	32.7	11225	0.0084	0.703548	12	0.7035	100	374	0.1618	0.512863	6	6.04	0.11	14.2	854	0.0024	0.282814	4	9.05	0.14	
KB-1	Eud-R														14.2	856	0.0024	0.282820	5	9.26	0.18	
KB-1	Tit	5.47	5042	0.0031	0.703288	15	0.7033	153	877	0.1052	0.512691	12	5.37	0.24								
KB-1	Ap	4.01	115630	0.0001	0.703324	11	0.7033	305	2495	0.0738	0.512644	7	5.93	0.14								
KB-3	Eud-1	12.0	8724	0.0040	0.703412	29	0.7034	80	284	0.1702	0.512874	10	5.86	0.19	14.2	1243	0.0016	0.282811	6	9.14	0.21	
KB-3	Eud-1R														15.0	1252	0.0017	0.282812	6	9.15	0.20	
KB-3	Eud-2	11.9	8832	0.0039	0.703397	16	0.7034	80	285	0.1699	0.512919	15	6.76	0.29	13.4	1270	0.0015	0.282808	7	9.05	0.25	
KB-3	Eud-2R														16.9	1272	0.0019	0.282810	6	9.03	0.21	
KB-3	Ap-1	0.55			0.703357	20		253	1913	0.0799	0.512632	10	5.41	0.20								
KB-3	Ap-2	13.4	51806	0.0008	0.703301	23	0.7033	229	1704	0.0812	0.512628	12	5.27	0.24								
KB-3	Ap-3	49.9	70067	0.0021	0.703316	12	0.7033	204	1551	0.0794	0.512641	8	5.61	0.17								
LV13	Eud	16.1	17682	0.0026	0.703690	15	0.7037	724	2752	0.1591	0.512775	8	4.45	0.16	45.7	1317	0.0049	0.282741	4	5.83	0.14	
LV01	Eud-1	6.56	11480	0.0017	0.703911	11	0.7039	492	2541	0.1170	0.512706	11	5.10	0.21	31.7	1674	0.0027	0.282764	5	7.22	0.18	
LV01	Eud-1R				0.703926	16					0.512714	10			31.7	1674	0.0027	0.282768	5	7.33	0.18	
LV01	Eud-1R														31.7	1682	0.0027	0.282770	4	7.40	0.14	
LV01	Eud-2	6.38	12088	0.0015	0.703930	15	0.7039	489	2499	0.1184	0.512687	11	4.66	0.21	32.4	1620	0.0028	0.282751	4	6.70	0.13	
LV01	Eud-2R														32.4	1629	0.0028	0.282752	5	6.75	0.18	
SM06	Eud	6.90	28133	0.0007	0.708506	13	0.7085	251	1098	0.1384	0.511928	9	−12.18	0.18	28.5	1500	0.0027	0.282334	3	−10.96	0.12	
SM06	Eud-R														28.5	1505	0.0027	0.282335	4	−10.92	0.14	
SM06	Tit	1.9	5062	0.0011	0.708338	11	0.7083	178	1054	0.1020	0.511876	10	−12.15	0.19								
TMZ177	Eud	21.1	13623	0.0045	0.703252	17	0.7032	47	504	0.0569	0.512836	10	4.65	0.19	7.92	841	0.0013	0.282933	9	6.62	0.32	
TMZ177	Eud-R														7.92	841	0.0013	0.282936	7	6.74	0.25	
MSH52	Eud	24.1	731	0.0954	0.704307	14	0.7041	543	3620	0.0908	0.512804	8	4.99	0.16	83.4	1748	0.0068	0.283059	11	12.41	0.41	
MSH52	Eud														83.4	1737	0.0068	0.283056	11	12.33	0.39	
MSH52	Eud														83.4	1742	0.0068	0.283054	7	12.23	0.25	
KPW	Eud	37	1237	0.087	0.740378	24	0.7391	756	2198	0.2079	0.512205	6	−9.90	0.12	257	960	0.0380	0.282692	3	−6.06	0.11	
LGS	Eud	13.8	1776	0.0224	0.703934	13	0.7039	223	1519	0.0888	0.512648	13	3.77	0.26	49.8	1912	0.0037	0.282828	3	7.07	0.11	
LGS	Eud-R1														49.8	2046	0.0035	0.282841	3	7.58	0.11	
LGS	Eud-R2														49.8	1960	0.0036	0.282837	4	7.39	0.14	

$0.70394 \pm 8$  (2SD,  $n=4$ ) (Fig. 1), identical to that obtained by laser ablation within errors.

For Nd isotopes, larger spot sizes of 80, 120 and 160  $\mu\text{m}$  and repetition pulse rates of 4, 6 and 8 Hz were used. These data yield a weighted average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.512691 \pm 28$  (2SD,  $n=90$ ) (Fig. 1b, Table 1). The obtained average  $^{145}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.348410 \pm$

$16$  (2SD,  $n=90$ ) is identical to the theoretical value of 0.348415 within error. In common with the Sr isotopic analyses, there are no significant variations for the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios obtained under different spot sizes with different pulse rates. Using the solution method, LV01 has a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.512701 \pm 24$  (2SD,  $n=4$ ) with  $^{147}\text{Sm}/^{144}\text{Nd}$  of 0.1173 (Fig. 1), consistent with the laser ablation data.

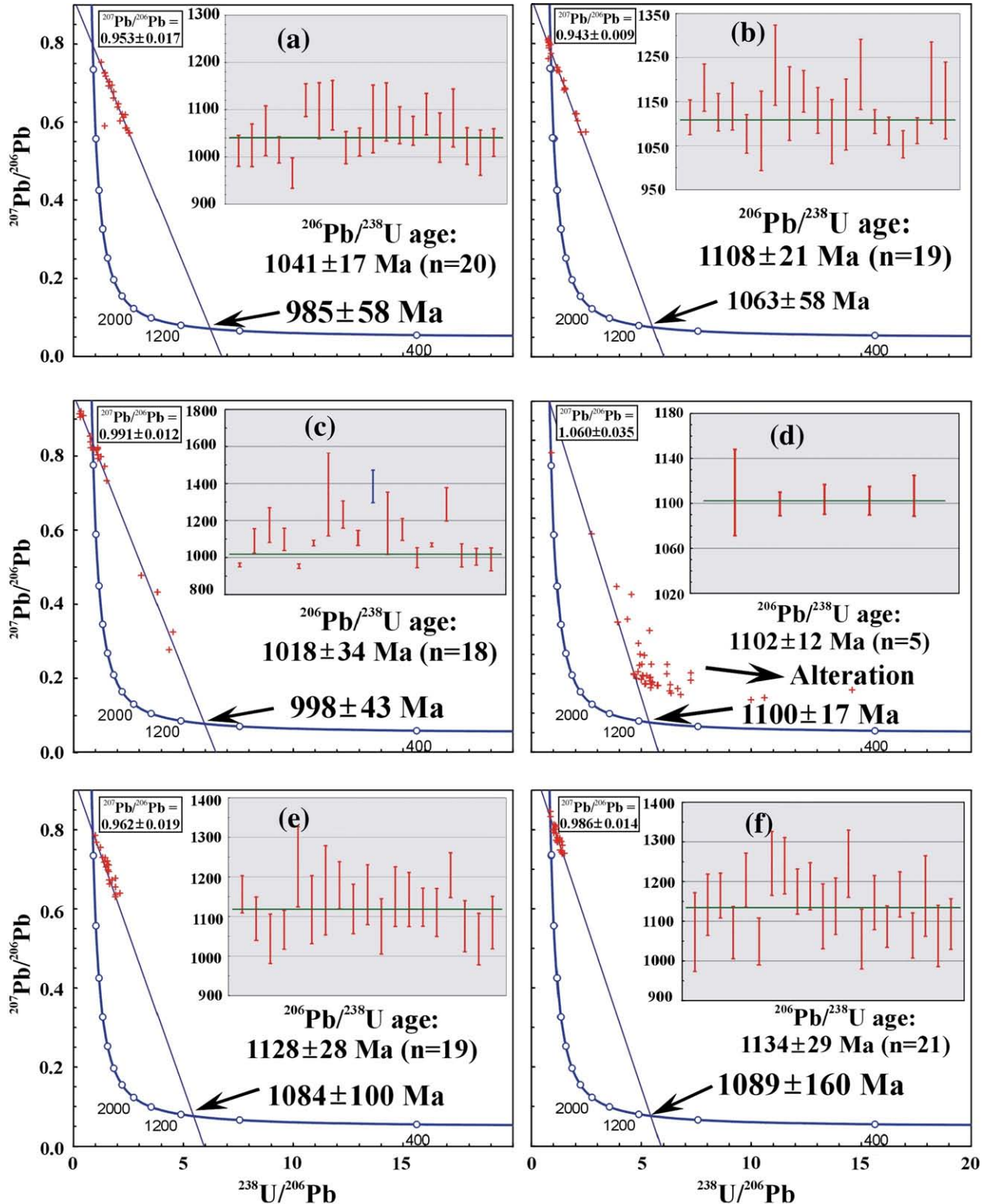


Fig. 2. U–Pb ages and common Pb isotopic composition of eudialyte from the Ilímaussaq complex, Greenland. (a) GM1370; (b) GM1369; (c) KP21; (d) KP58; (e) GM1335 and (f) ILM101.

For Hf isotopes, spot sizes of 80, 120 and 160  $\mu\text{m}$  and repetition pulse rates of 4, 6, 8 and 10 Hz were used. All analyses yield a weighted average  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282765 \pm 59$  (2SD,  $n = 120$ ), which is identical to the solution value of  $0.282761 \pm 18$  (2SD,  $n = 5$ , Fig. 1c, Table 1).  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios obtained with large spot sizes and high pulse rates are more precise than those obtained with smaller spot sizes and low repetition rates. The average  $^{178}\text{Hf}/^{177}\text{Hf}$  ratio is  $1.467246$  (2SD,  $n = 120$ ), identical to the theoretical value of 1.8867 within error.

In summary, laser ablation of LV01 gives identical Sr, Nd and Hf isotopic ratios compared to those obtained by solution technique within analytical errors (Fig. 1, Table 1), indicating that our analytical protocol is reliable. Thus, eudialyte LV01 was used for external correction during *in situ* laser ablation analysis for Sr, Nd and Hf isotopic compositions.

#### 4. Applications

In this study, eudialytes from nine apgaitic complexes were investigated. The descriptions of samples and their host complexes are given in the Appendix A. Representative major and trace element compositions of the eudialytes from the different samples are given in Table 2. As the focus of this work is determination of the isotopic composition of eudialyte we have not followed the detailed major element nomenclature of eudialyte group minerals as proposed by Johnsen et al. (2003), and refer to the material investigated simply as eudialyte (*sensu lato*). The *in situ* Sr, Nd and Hf isotopic data for the analysed eudialytes, together with apatites and titanites from the same samples, are summarized in Table 3. In order to check the reliability of our data, some minerals (eudialyte, apatite and titanite) were selected for solution analysis; these data are given in Table 4.

##### 4.1. Ilímaussaq syenite, Greenland

In the Tera–Wasserburg concordia diagrams (Fig. 2), eudialytes from Ilímaussaq have high common Pb contents. With the exception of KP58, the lower intercept ages range from  $985 \pm 58$  (GM1370) to  $1089 \pm 160$  (ILM101) Ma. Using the common Pb composition determined by the upper intercept, the  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  weighted ages vary from  $1018 \pm 34$  (KP21) to  $1134 \pm 29$  (ILM101) Ma (Fig. 2). Eudialyte from sample KP58 shows a significant deviation from the  $\sim 1100$  Ma discordia line, indicating Pb loss due to later alteration. However, five analyses of the least altered areas define a line with a lower intercept age of  $1100 \pm 17$  Ma, and  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  weighted age of  $1102 \pm 12$  Ma (Fig. 2d). Considering that ILM101 is a late aplite dyke, it is concluded that the Ilímaussaq complex was emplaced before  $\sim 1134$  Ma. The above ages were calculated from  $^{206}\text{Pb}/^{238}\text{U}$  ratios. For Precambrian minerals, the  $^{207}\text{Pb}/^{206}\text{Pb}$  age is usually used as later Pb loss would result in “younging” of the  $^{206}\text{Pb}/^{238}\text{U}$  age, but not the  $^{207}\text{Pb}/^{206}\text{Pb}$  age. However, the high common Pb content makes it impossible to calculate the  $^{207}\text{Pb}/^{206}\text{Pb}$  age in this study as a  $^{207}\text{Pb}$  correction was used. Therefore, the present data support the conclusion that the emplacement of Ilímaussaq complex took place at  $\sim 1160$  Ma, as constrained by the baddeleyite and zircon U–Pb ages of the earlier augite syenite and alkali granite, respectively (Upton et al., 2003; Krumrei et al., 2006).

Most of the samples have relatively high Rb/Sr ratios of 0.012 to 0.174 (Table 2), hence it is not possible to determine Sr isotopic compositions by *in situ* analysis as samples with  $\text{Rb}/\text{Sr} > 0.02$  cannot be accurately corrected for the Rb interference (Yang et al., 2009). Using 160  $\mu\text{m}$  size of laser spot, the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio for eudialyte in GM1369 is  $0.7085 \pm 3$  with an  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio of  $0.019 \pm 1$  ( $n = 8$ , Fig. 3a), confirming the previous conclusion that the Ilímaussaq complex has a high initial Sr isotopic composition of  $\sim 0.71$  (Blaxland et al., 1976; Waight et al., 2002).

The Nd isotopic analyses show significant variations in  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, located along the reference line of 1160 Ma (Fig. 3b). The  $\epsilon_{\text{Nd}}(t)$  values range from  $-2.7 \pm 0.4$  to  $-1.2 \pm 0.2$ , and are

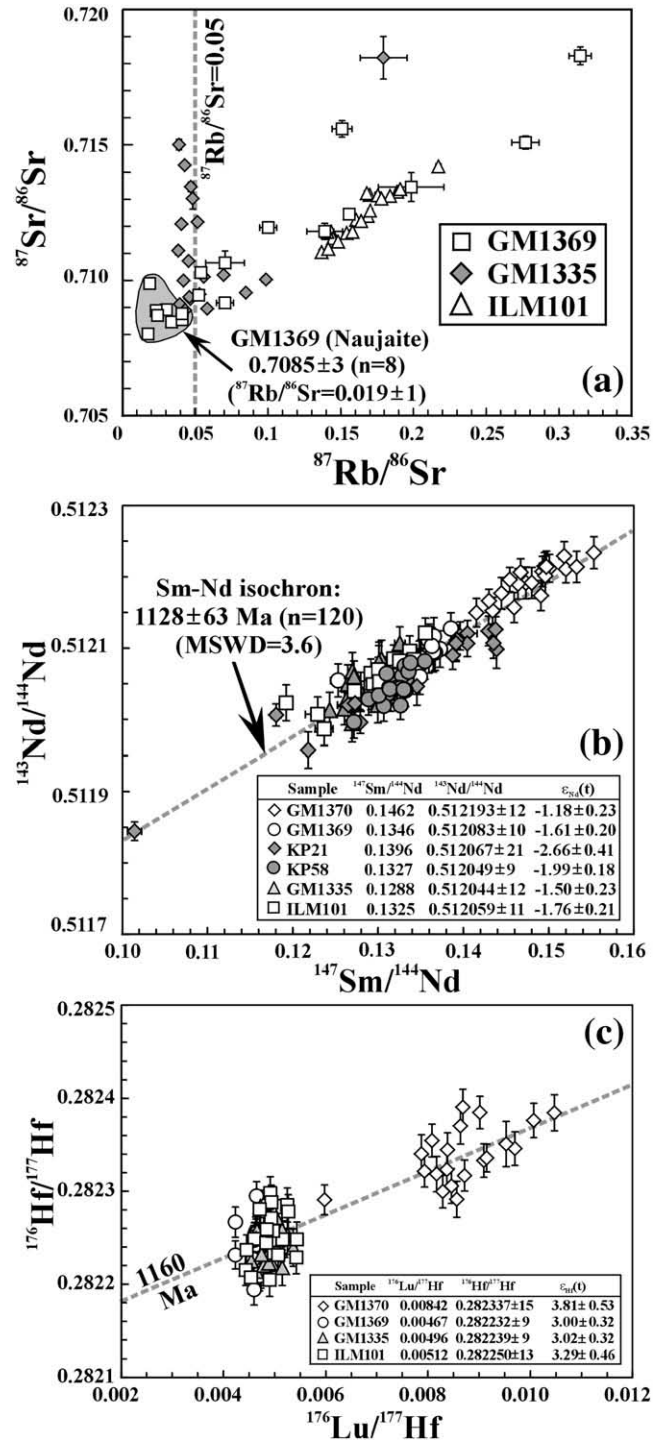


Fig. 3. Sr–Nd–Hf isotopic composition of eudialyte from the Ilímaussaq complex, Greenland. (a) Sr isotopic data; (b) Nd isotopic data; and (c) Hf isotopic data.

very similar to the published  $\epsilon_{\text{Nd}}(t)$  values of  $-3.6 \pm 0.5$  to  $+0.8 \pm 0.5$  obtained from whole-rock and mineral analyses (Blaxland et al., 1976; Paslick et al., 1993; Stevenson et al., 1997; Marks et al., 2004). Eudialytes from three samples (GM1370, KP21 and KP58) were also analysed by solution methods and gave similar  $\epsilon_{\text{Nd}}(t)$  values (between  $-2.0 \pm 0.1$  to  $-0.5 \pm 0.2$ ) compared to those obtained by laser ablation.

Principally, the high Hf concentrations of 1600–2201 ppm should make it possible to obtain precise Hf isotopic ratios for these samples. However, samples KP21 and KP58 have high Yb concentrations making it impossible to correct for the interferences of  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$  during *in situ* laser ablation analysis (see above). The other samples



have  $\varepsilon_{\text{Hf}}(t)$  values ranging from  $+3.0 \pm 0.5$  to  $+3.8 \pm 0.5$  (Fig. 3c), identical to the value of  $+4.3 \pm 0.7$  obtained by Patchett et al. (1981). Similarly, the  $\varepsilon_{\text{Hf}}(t)$  values obtained from the solution data ( $+5.4 \pm 1.0$ ) are comparable to those by laser ablation.

#### 4.2. Khibiny syenite, Kola Peninsula, Russia

Eudialytes from Khibiny have higher Sr (6575–10579 ppm), and lower Rb (4.7–25 ppm), Sm (77–123 ppm), Nd (235–486 ppm) and Lu (18–22 ppm) concentrations than those from the Ilímaussaq complex. In the Tera–Wasserburg U–Pb diagram (Fig. 4), the lower intercept ages for eudialytes are from  $354 \pm 27$  to  $365 \pm 23$  Ma, with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages from  $356 \pm 11$  to  $365 \pm 10$  Ma. For sample KB-0, however, if data for titanite and apatite are combined with the eudialyte data, the lower intercept and  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages are  $368 \pm 11$  and  $368 \pm 5$  Ma (Fig. 4a). Similarly, for sample KB-1, the combined analyses of eudialyte, titanite and apatite yield a lower intercept age of  $363 \pm 15$  Ma, and a  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  age of  $361 \pm 6$  Ma (Fig. 4b). Additionally, analyses of eudialyte and apatite with one exception from sample KB-3 yield lower intercept and  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $369 \pm 20$  and  $365 \pm 8$  Ma (Fig. 4d). These age data are consistent with those previously obtained by zircon U–Pb, whole-rock Rb–Sr and mineral Ar–Ar methods (Kramm et al., 1993; Kramm and Kogarko, 1994; Arzamastsev et al., 2007).

In contrast to the Ilímaussaq complex, eudialytes from Khibiny have much high Sr contents (6575–10579 ppm) with low Rb/Sr ratios

(0.0006 to 0.0023) and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios varying from  $0.70339 \pm 1$  to  $0.70350 \pm 2$ . Titanite and apatite have slightly lower  $^{87}\text{Rb}/^{86}\text{Rb}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than those of eudialyte from the same samples; an observation verified by solution analyses (Fig. 5a, Table 4).

Eudialytes from Khibiny show significant variations of  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios located along the reference line of 370 Ma (Fig. 5b), the age of emplacement of the complex. The  $\varepsilon_{\text{Nd}}(t)$  values show a narrow variation from  $+5.0 \pm 0.2$  to  $+5.7 \pm 0.2$ . Titanite and apatite (from samples KB-0, KB-1 and KB-3) have slightly lower  $\varepsilon_{\text{Nd}}(t)$  values than eudialytes from the same samples (Fig. 5b).

With Hf concentrations of 1221–1646 ppm and Lu/Hf and Yb/Hf ratios of 0.011–0.014 and 0.074–0.107, analyses yield  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic ratios from  $0.282797 \pm 9$  to  $0.282806 \pm 9$  and  $\varepsilon_{\text{Hf}}(t)$  values from  $+8.7 \pm 0.3$  to  $+9.0 \pm 0.3$  (Fig. 5c). In common with the Nd isotopes, all these analyses show some variation in the  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios, and located along the 370 Ma reference line (Fig. 5c). Therefore, our Sr, Nd and Hf isotopic data (initial Sr isotopes: 0.70339–0.70350;  $\varepsilon_{\text{Nd}}(t)$  values:  $+5.0$  to  $+5.7$ ;  $\varepsilon_{\text{Hf}}(t)$  values:  $+8.7$  to  $+9.0$ ) are closely compatible to the literature data (initial Sr isotopes: 0.7030–0.7043;  $\varepsilon_{\text{Nd}}(t)$  values:  $+1.3$  to  $+6.0$ ;  $\varepsilon_{\text{Hf}}(t)$  values:  $+8.0$  to  $+9.0$ ; Patchett et al., 1981; Kramm et al., 1993; Kramm and Kogarko, 1994; Barfod et al., 2003; Downes et al., 2005; Kogarko et al., 2008; Lahaye et al., 2008a,b).

#### 4.3. Lovozero syenite, Kola Peninsula, Russia

In contrast to eudialytes from Khibiny, those from Lovozero have much higher contents of Sr (10289–17928 ppm), Sm (503–881 ppm)

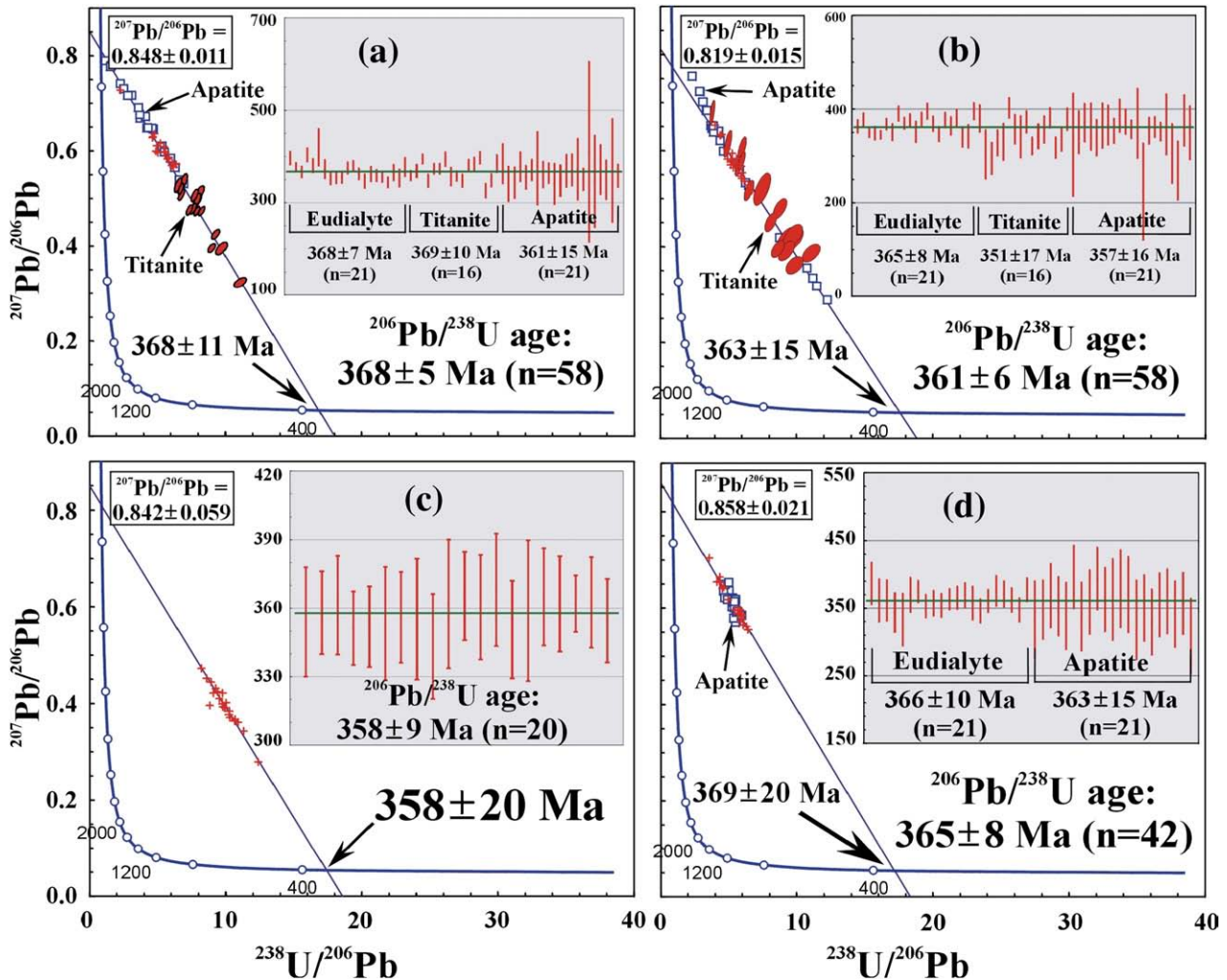


Fig. 4. U–Pb ages and common Pb isotopic composition for eudialyte from the Khibiny complex, Russia. (a) KB-0; (b) KB-1; (c) KB-2 and (d) KB-3.

and Nd (2815–3887 ppm) (Table 2). U–Pb analyses for Lovozero eudialytes yield lower intercept ages from  $357 \pm 20$  to  $377 \pm 88$  with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $359 \pm 8$  to  $376 \pm 6$  (Fig. 6). The average  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  age from the five samples is  $370 \pm 10$  Ma (Fig. 6f), identical to that of Khibiny within analytical errors.

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios range from  $0.70378 \pm 1$  to  $0.70404 \pm 1$  with  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios from 0.00208 to 0.00353 (Fig. 7a).  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratios vary from  $0.512662 \pm 8$  to  $0.512739 \pm 6$  with  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios from 0.1212 to 0.1641 and  $\epsilon_{\text{Nd}}(t)$  values from  $+3.5 \pm 0.1$  to  $+4.1 \pm 0.1$  (Fig. 7b).  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic ratios vary from  $0.282741 \pm 9$  to  $0.282790 \pm 13$  with  $\epsilon_{\text{Hf}}(t)$  values from  $+6.2 \pm 0.3$  to  $+8.1 \pm 0.5$  (Fig. 7c). Therefore, our Sr,

Nd and Hf isotopic data are closely compatible to the literature data (initial Sr isotopes: 0.7033–0.7041;  $\epsilon_{\text{Nd}}(t)$  values:  $+2.9$  to  $+4.9$ ;  $\epsilon_{\text{Hf}}(t)$  values:  $+5$  to  $+8$ ; Kramm et al., 1993; Kramm and Kogarko, 1994; Downes et al., 2005; Kogarko et al., 2008; Kogarko et al., 2010; Lahaye et al., 2008a,b).

4.4. Saima syenite, China

In contrast to eudialyte from the Ilímaussaq, Khibiny and Lovozero complexes, the samples from the Saima complex have higher Sr (22514–27323 ppm) and Hf (2235–2510 ppm) (Table 2). In the Tera–Wasserburg U–Pb diagrams, the lower intercept age of sample SM06 is  $217 \pm 39$  Ma with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $220 \pm 15$  Ma (Fig. 8a). When combined with data for associated titanite, the above two ages are identical at  $223 \pm 4$  Ma (Fig. 8a). Interestingly, sample SM07 shows a large range of Pb isotopic variations, which yield a precise lower intercept age of  $224 \pm 5$  Ma with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $224 \pm 4$  Ma (Fig. 8b). Both ages are identical to the zircon U–Pb age of  $225 \pm 1$  Ma, obtained from the nearby eudialyte-free nepheline syenite (Wu, unpublished data). Sample SM25 gives a younger lower intercept age of  $193 \pm 4$  Ma with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $193 \pm 3$  Ma (Fig. 8c). This young age is considered to result from Pb loss, which is supported by a petrographically observed alteration (see Appendix A).

Rb/Sr ratios vary between 0.00023 and 0.00027,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vary in a narrow range from  $0.70854 \pm 3$  to  $0.70857 \pm 2$  (Fig. 8d), consistent with previously reported whole-rock data (Jing et al., 1995; Chen, 1996; Zhou et al., 1996). The  $\epsilon_{\text{Nd}}(t)$  values range from  $-12.3 \pm 0.2$  to  $-12.7 \pm 0.2$  (Fig. 8e). In addition, titanite from SM06 yields similar Sr–Nd isotopic data. The  $\epsilon_{\text{Hf}}(t)$  values range from  $-11.4 \pm 0.3$  to  $-10.4 \pm 0.4$  (Fig. 8f). In contrast to the Ilímaussaq and Khibiny samples, there are less significant Sr–Nd isotopic variations among the eudialytes from different samples, suggesting that alteration did not modify the Sr–Nd–Hf isotopic systems.

4.5. Tamazeght complex, Morocco

U–Pb analyses of Tamazeght eudialytes yield lower intercept ages of  $39 \pm 9$  Ma for TM177,  $50 \pm 105$  Ma for TM241 and  $46 \pm 95$  Ma for TM298 in the Tera–Wasserburg diagrams (Fig. 9), with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $40 \pm 5$ ,  $43 \pm 35$ , and  $43 \pm 24$  Ma (Fig. 9a, b, c). The latter two ages are highly imprecise due to the low amounts of radiogenic Pb, but still agree with the age of  $\sim 44$  Ma (Marks et al., 2008a,b). Eudialytes from this complex have high Sr concentrations of 14132–25699 ppm with Rb/Sr ratios of 0.0006–0.0019 and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios range from  $0.70320 \pm 2$  to  $0.70326 \pm 3$  (Fig. 9d), only slightly lower than 0.7033–0.7035 obtained by Marks et al. (2009) from whole-rock data of other samples in the complex. The eudialytes have  $\epsilon_{\text{Nd}}(t)$  values between  $+4.0 \pm 0.1$  and  $+4.6 \pm 0.3$  (Fig. 9e), slightly higher than  $+2.0$ – $+4.1$  obtained by Marks et al. (2009) from whole-rock analyses. The obtained  $\epsilon_{\text{Hf}}(t)$  values vary from  $+4.5 \pm 0.2$  to  $+5.9 \pm 0.3$  (Fig. 9f).

4.6. Mont Saint Hilaire, Canada

In the Tera–Wasserburg U–Pb diagram (Fig. 10a, b), the lower intercept ages are  $137 \pm 35$  (MSH38) and  $137 \pm 60$  (MSH58) Ma, with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $128 \pm 12$  (MSH38) and  $132 \pm 16$  (MSH52) Ma. These ages are identical to the zircon age of  $141 \pm 7$  Ma reported by Cox and Wilton (2006). In common with the Ilímaussaq complex, eudialyte from MSH52 has a high Rb/Sr ratio of 0.14, making *in situ* laser ablation analysis impossible. However, for MSH38, the  $^{87}\text{Rb}/^{86}\text{Rb}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios are 0.00580 and 0.70385  $\pm$  3 (Fig. 11a), comparable to the whole-rock data (Currie et al., 1986). The  $\epsilon_{\text{Nd}}(t)$  values for the two eudialytes are  $+4.4 \pm 0.2$  and  $+5.0 \pm 0.1$  and the  $\epsilon_{\text{Hf}}(t)$  values are  $+11.6 \pm 0.5$  and  $+8.4 \pm 0.5$ , respectively (Fig. 11b, c).

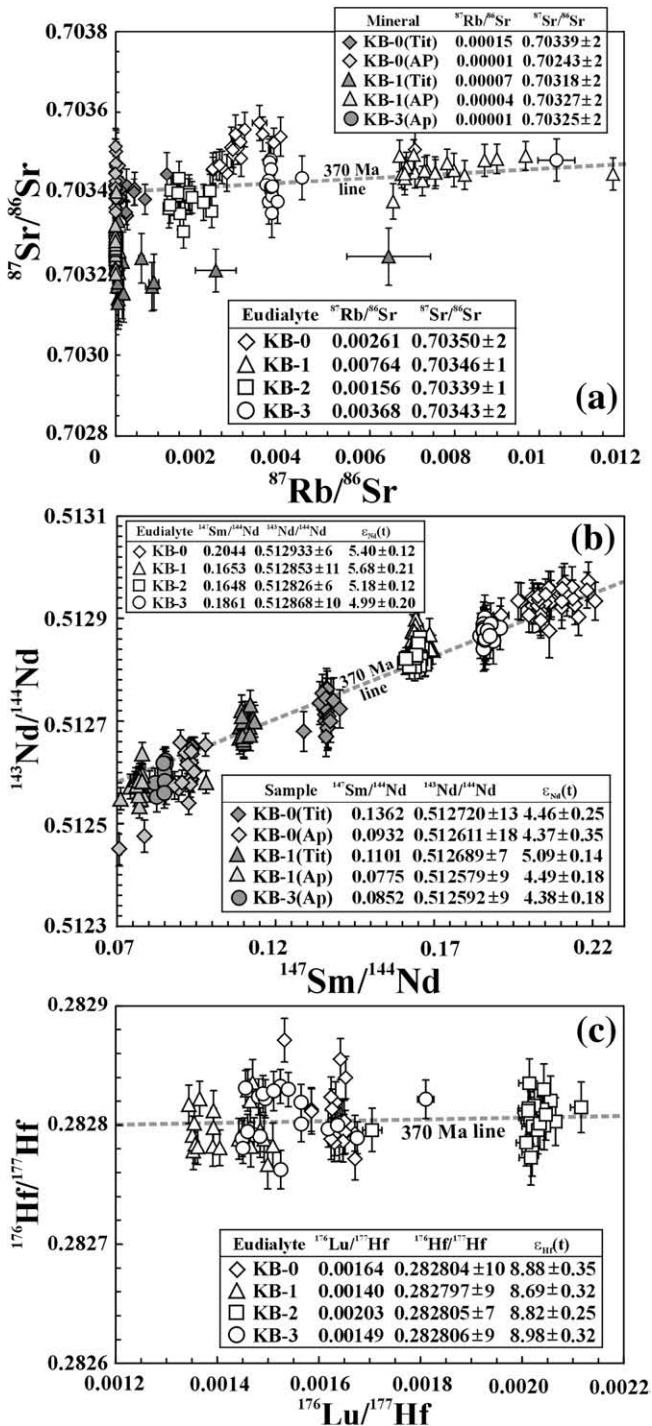


Fig. 5. Sr–Nd–Hf isotopic composition for eudialyte from the Khibiny complex, Russia. (a) Sr isotopic data; (b) Nd isotopic data; and (c) Hf isotopic data.

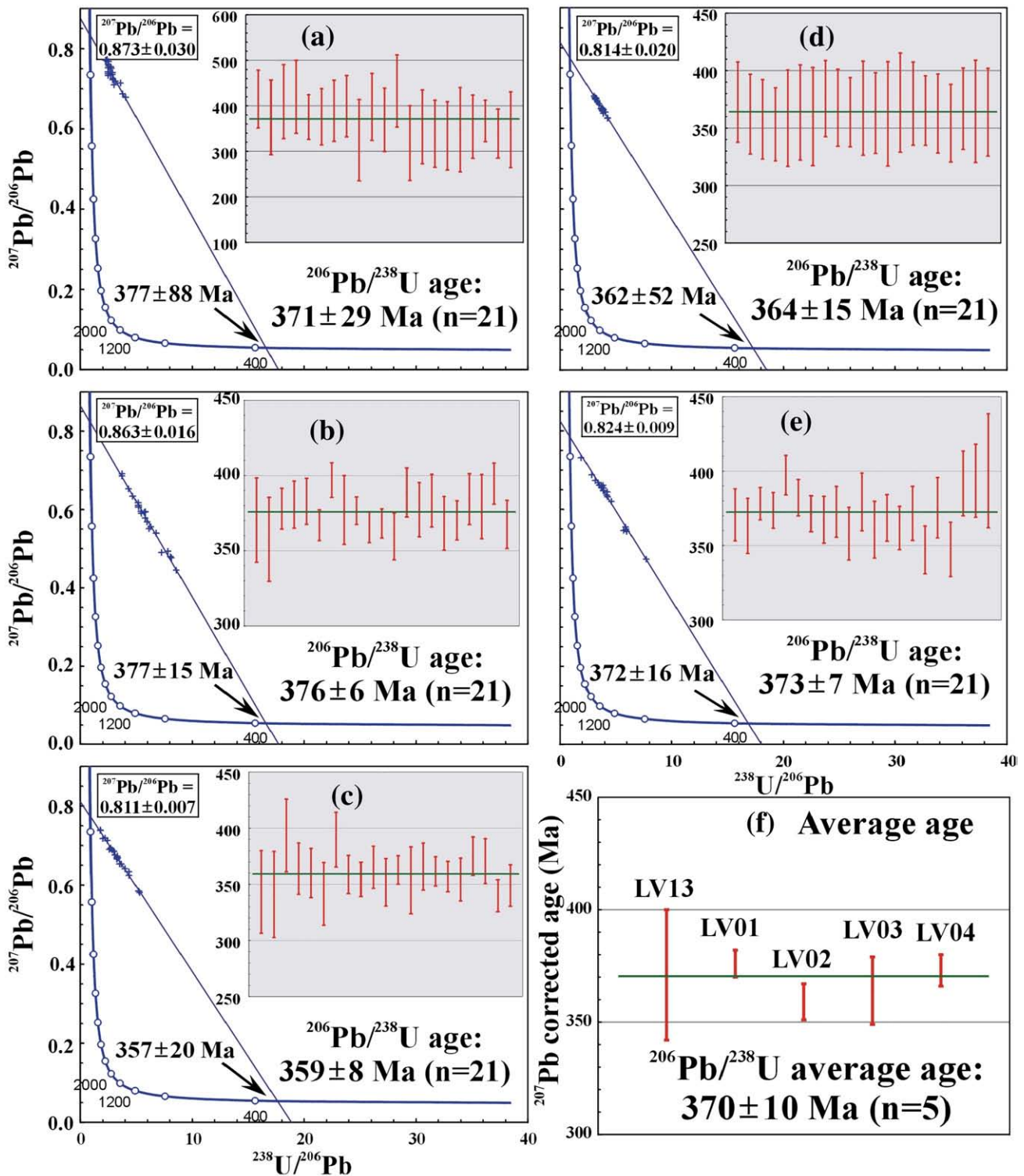


Fig. 6. U–Pb ages and common Pb isotopic composition for eudialyte from the Lovozero complex in Kola of Russia. (a) LV13; (b) LV01; (c) LV02; (d) LV03, (e) LV04 and (f) average age of the above five samples.

#### 4.7. Other localities

##### 4.7.1. Poços de Caldas

Due to high common lead contents, eudialyte (PDC) from this locality yield an imprecise lower intercept age of  $78 \pm 23$  Ma. The  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  age is  $77 \pm 13$  Ma (Fig. 12a). The Rb/Sr and Lu/Hf ratios are of

0.002 and 0.007, respectively. The  $^{87}\text{Rb}/^{86}\text{Rb}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{147}\text{Sm}/^{144}\text{Nd}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic ratios are 0.00457, 0.70529  $\pm$  0.00851, 0.512413  $\pm$  6, 0.0025, and 0.282653  $\pm$  11, with  $\epsilon_{\text{Nd}}(t)$  and  $\epsilon_{\text{Hf}}(t)$  values of  $-3.3 \pm 0.2$  and  $-2.5 \pm 0.4$  (Fig. 12 d, e, f), in which the Sr–Nd isotopic data are comparable to the associated nepheline syenites (Shea, 1992).

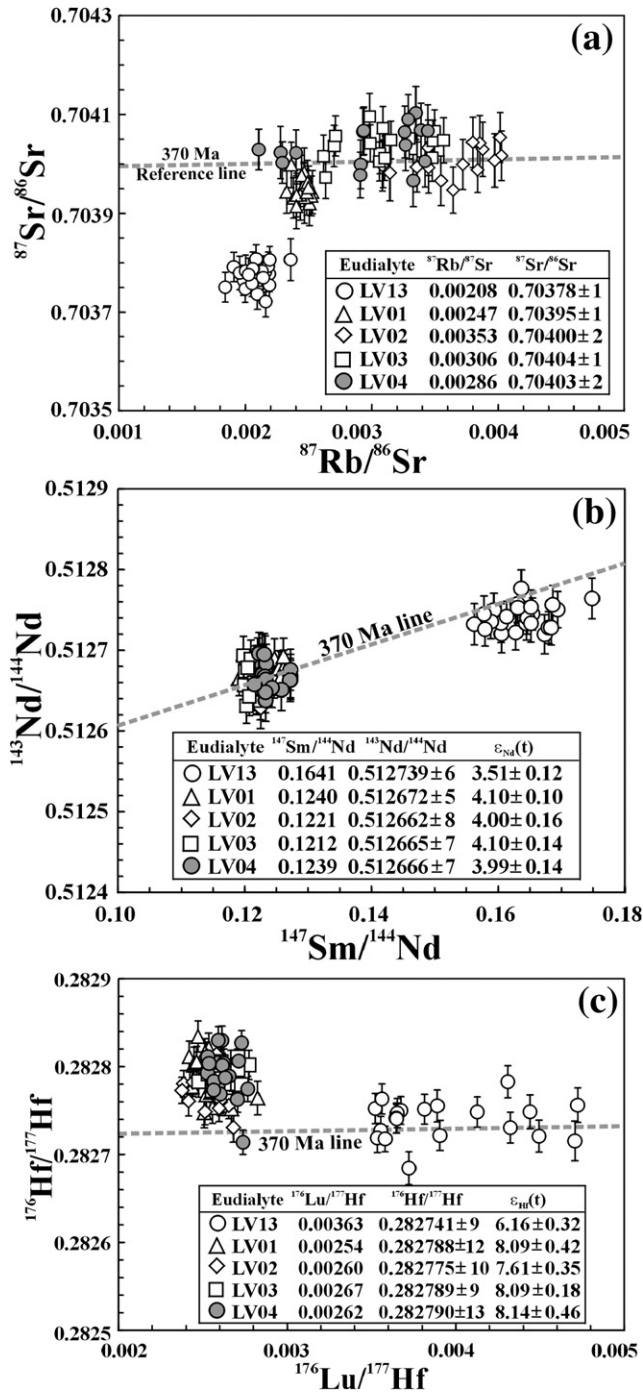


Fig. 7. Sr–Nd–Hf isotopic composition for eudialyte from the Lovozero complex, Kola, Russia. (a) Sr isotopic data; (b) Nd isotopic data; and (c) Hf isotopic data.

#### 4.7.2. Kipawa

In the Tera–Wasserburg U–Pb diagram (Fig. 12b), the lower intercept ages are  $1014 \pm 61$  Ma, with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $1012 \pm 16$  Ma for eudialyte (KPW) from this locality. The high Rb/Sr ratio of 0.03 makes *in situ* laser ablation analysis impossible. The sample has an average Lu content of 577 ppm, which corresponds to a  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of  $\sim 0.04$ ; much higher than those of other samples and making accurate measurement of the  $^{176}\text{Hf}/^{177}\text{Hf}$  impossible by laser ablation techniques. Using a 120  $\mu\text{m}$  spot size, the  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratios are 0.2438 and  $0.512403 \pm 6$ , with  $\epsilon_{\text{Nd}}(t)$  value of  $10.6 \pm 0.1$  (Fig. 12e). However, this eudialyte shows some Sm/Nd isotopic

variations, which yield an imprecise isochron with age of  $965 \pm 75$  Ma (Fig. 12e), identical to the U–Pb age within analytical errors. Solution analysis of this sample gives an  $\epsilon_{\text{Hf}}(t)$  value of  $-6.1 \pm 0.1$  and a  $\epsilon_{\text{Nd}}(t)$  value of  $-9.9 \pm 0.1$ , the latter of which is similar to that obtained by laser ablation.

#### 4.7.3. Langesund Fjord, Norway

Because of its high common lead contents (472 ppm Pb), this sample (LGS) cannot be used to obtain reasonable U–Pb ages (Fig. 12c). However, the apatite from this sample exhibits considerable Pb isotopic variations, which yield a lower intercept age of  $261 \pm 6$  Ma, with  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $260 \pm 4$  Ma (Fig. 12c). This age is in accord with the age data of Corfu and Dahlgren (2008) and Larsen et al. (2008).

In contrast to other complexes, eudialyte from this sample has a Sr content of 2409 ppm, and the high REE concentrations, hence significant interference, makes the Sr isotopic determination by laser methods impossible (see below). Using a 120  $\mu\text{m}$  spot size, the  $^{147}\text{Sm}/^{144}\text{Nd}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic ratios are 0.0847,  $0.512610 \pm 6$ , 0.00246 and  $0.282833 \pm 7$ , with  $\epsilon_{\text{Nd}}(t)$  and  $\epsilon_{\text{Hf}}(t)$  values of  $+3.2 \pm 0.1$  and  $+7.5 \pm 0.3$  (Fig. 12f). Apatite from this sample gives  $^{87}\text{Rb}/^{86}\text{Rb}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratios are 0.00029,  $0.70366 \pm 2$ , 0.0913 and  $0.512667 \pm 18$ , with  $\epsilon_{\text{Nd}}(t)$  value of  $+4.1 \pm 0.4$  (Fig. 12d). These Sr–Nd–Hf isotopic data are closely consistent to those reported for the hosted Larvik batholith (Neumann et al., 1988; Rasmussen et al., 1988; Dahlgren et al., 1996). For example, zircon  $\epsilon_{\text{Hf}}(t)$  values of  $+6.7$  to  $+5.5$  by Dahlgren et al. (1996) from the Larvik batholith are excellently coincided with the present data.

## 5. Discussion

### 5.1. Compositional variation of eudialyte

Data obtained in this study by laser ablation method permit comparisons of the trace element and isotopic composition of eudialyte from diverse localities. Fig. 13 shows that the distribution pattern of REE and other trace elements obtained in present study, three subgroups of eudialyte exist (Fig. 13). In common with their host rocks (Kramm and Kogarko, 1994; Tan et al., 1999; Arzamastsev et al., 2001, 2005), eudialytes from Khibiny, Lovozero and Saima have relatively low REE concentrations with no significant Eu and Sr anomalies (i.e. the high Sr subgroup in Fig. 13a, b). Eudialyte from the Lovozero has the highest REE contents with weak positive Eu anomalies. In contrast, eudialytes from Ilmaussaq, Mont Saint Hilaire, Kipawa and Langesund Fjord display well-defined negative Eu anomalies coupled with Sr depletion (i.e. the low Sr subgroup on Fig. 13c, d). Similar features are evident in the host rocks (Bailey et al., 2001, 2006; Sørensen et al., 2006). Eudialyte from the Tamazeght complex contains much less REE (i.e. the low REE subgroup in Fig. 13e, f). These groups suggest that eudialyte-bearing apgaitic rocks might have diverse origins and/or petrogenetic processes.

### 5.2. Eudialyte: potential for the U–Pb age determination of apgaitic rocks

U–Pb isotopic dating of zircon and baddeleyite is one of the most important methods for determining the age of emplacement of plutonic rocks as these minerals have high U contents, low amounts of common Pb, and high closure temperatures. However, this method cannot be typically used for the apgaitic rocks as Zr is highly soluble in this type of magma, precluding the crystallization of zircon and/or baddeleyite. Thus, apgaitic rocks are characterized by occurrence of the zirconium-rich minerals such as eudialyte and lavenite etc. To date the potential of eudialyte as a U–Pb geochronometer has not been investigated.

According to our study, eudialyte has U concentrations of 16–1249 ppm (Fig. 14a), which make it possible to determine precisely

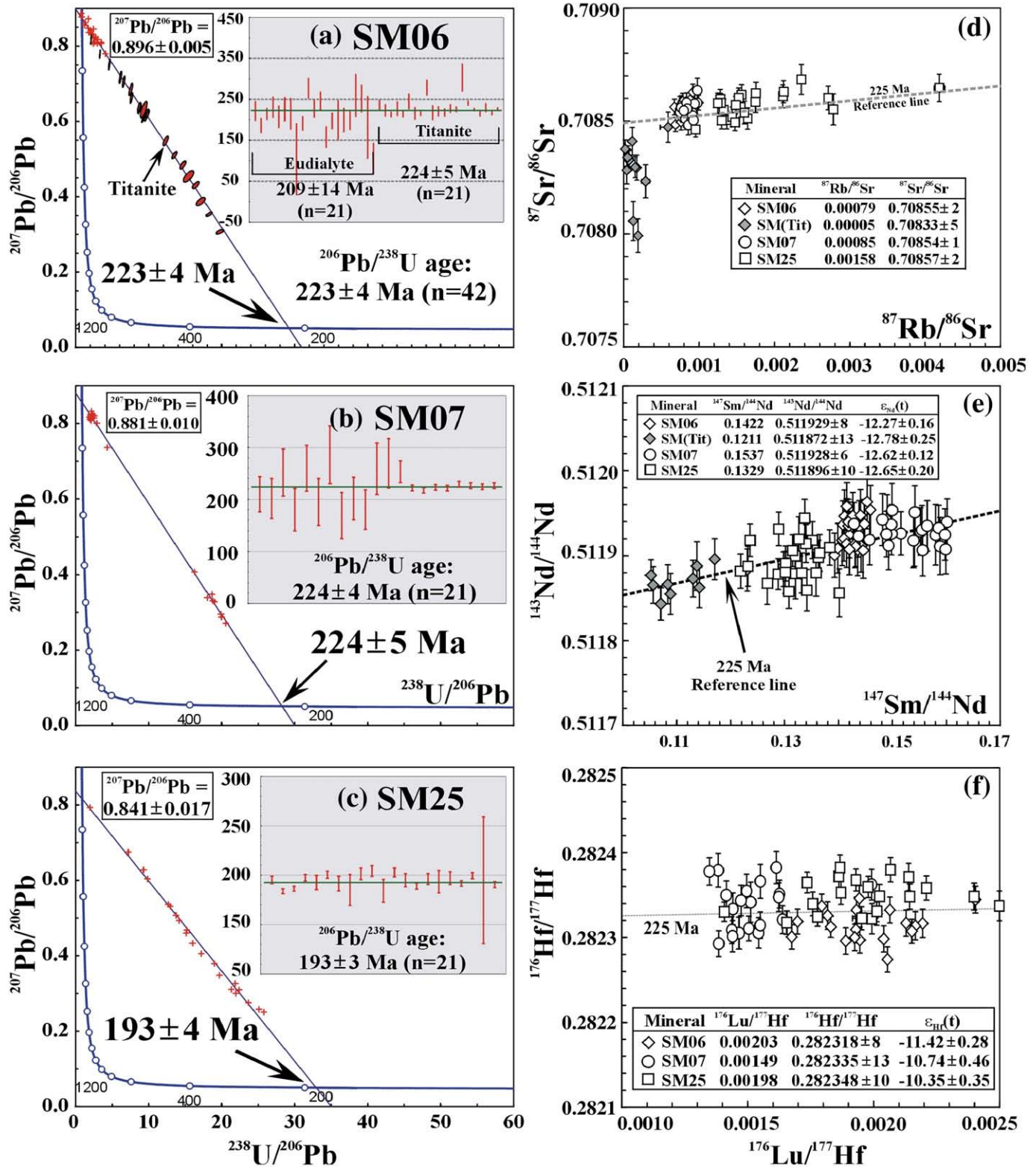


Fig. 8. U–Pb ages, common Pb and Sr–Nd–Hf isotopic composition for eudialyte from the Saima complex in northeastern China. (a) SM06 (U–Pb); (b) SM07 (U–Pb); (c) SM25 (U–Pb); (d) Sr isotopic data; (e) Nd isotopic data; and (f) Hf isotopic data.

the U–Pb isotope composition, by either traditional TIMS or modern *in situ* techniques. However, several factors have to be considered if this mineral is to be used for geochronology. First, eudialyte is usually altered and replaced by secondary zircon, baddeleyite, catapleite,

zirconsalite, steenstrupine, wohlerite, mosandrite and other minerals (e.g., Coulson and Chambers, 1996; Coulson, 1997; Sørensen, 1997; Mitchell and Liferovich, 2006). In our studied samples, most eudialytes display only minor alteration. For example in sample

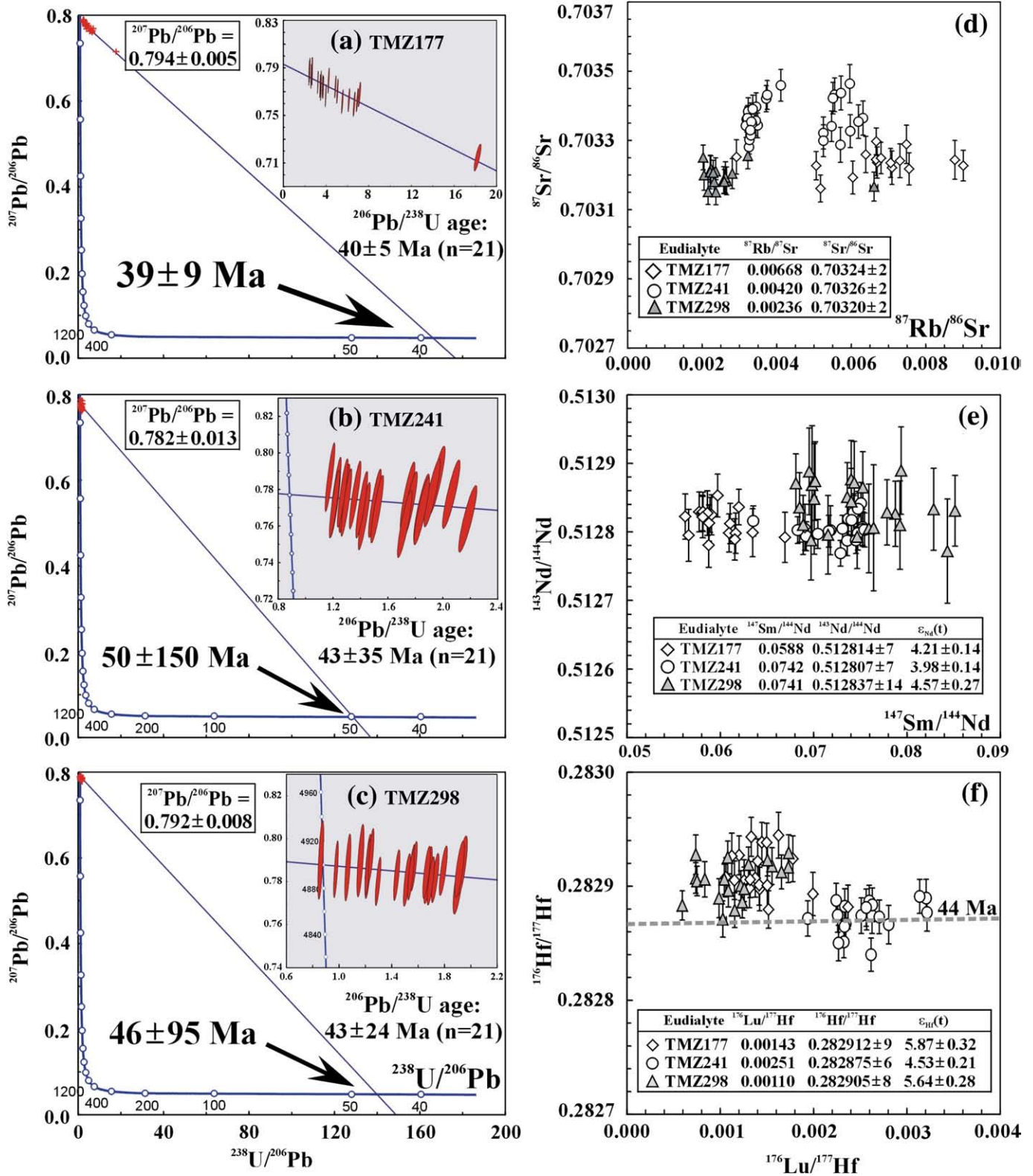


Fig. 9. U–Pb ages, common Pb and Sr–Nd–Hf isotopic composition for eudialyte from the Tamazeght complex in Morocco. (a) TMZ177 (U–Pb); (b) TMZ241 (U–Pb); (c) TMZ298 (U–Pb); (d) Sr isotopic data; (e) Nd isotopic data; and (f) Hf isotopic data.

LV13 from Lovozero, the eudialyte occurs as large euhedral crystals with oscillatory zoning, suggesting this is a primary feature of crystallization from magma (Kogarko et al., 1982; Sorensen, 1997). However, some grains of eudialyte from the Ilímaussaq, Saima and

Mont Saint Hilaire complexes have been altered along grain boundaries and fractures. Therefore, detailed petrographic observations are necessary before laser analyses, which also imply that *in situ* technique is the best method for U–Pb isotopic analyses.

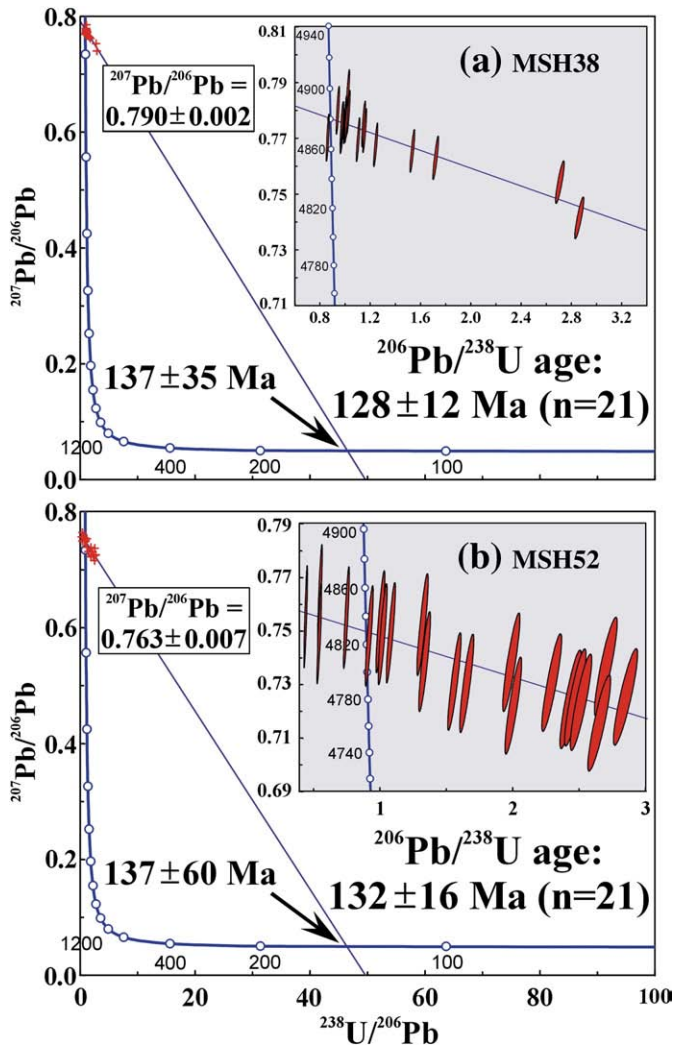


Fig. 10. U–Pb ages and common Pb isotopic composition for eudialyte from the Mont Saint Hilaire, Quebec, Canada. (a) MSH38; and (b) MSH52.

A second problem is with regard to is the eudialyte U–Pb closure temperature. It is commonly accepted that eudialyte is of primarily magmatic origin with crystallization temperature of  $\sim 860\text{--}720\text{ }^{\circ}\text{C}$  (Kogarko et al., 1982; Sørensen, 1997), which is supported by its euhedral habit, (Coulson and Chambers, 1996; Coulson, 1997; Pfaff et al., 2008). However, it is also known that eudialyte can be formed during the hydrothermal stage of apaitic magma evolution at temperatures of  $<350\text{ }^{\circ}\text{C}$  (e.g., Olivo and Williams-Jones, 1999; Schilling et al., 2009). Moreover, petrographic observations have indicated that this mineral is susceptible to alteration in the later stage of evolution of apaitic magmas (Olivo and Williams-Jones, 1999; Salvi et al., 2000; Mitchell and Liferovich, 2006; Sørensen, 2006); such alteration could disturb and reset the original U–Pb isotopic system.

In order to understand fully the U–Pb closure temperature of eudialyte, a theoretical calculation is illustrated Fig. 15. The kinetic-porosity model of Zhao and Zheng (2007) is applied for the calculation of diffusion coefficients, and the method of Dodson (1973) is used for calculation of the closure temperatures ( $T_c$ ). For comparison, the diffusion coefficients and closure temperatures of zircon and titanite are also included. From these data it is apparent that eudialyte has much more rapid Pb diffusion rate and lower closure temperatures than either zircon or titanite (Fig. 15). Assuming a cooling rate of  $100\text{ }^{\circ}\text{C}/\text{Ma}$ , a eudialyte of 10 mm grain-size (typical size of material

used in this study) has a U–Pb closure temperature of  $\sim 675\text{ }^{\circ}\text{C}$ , much lower than that of zircon and titanite of the same size (Fig. 15b). However, in our samples, the analysed titanite has commonly a grain-size of only  $\sim 100\text{ }\mu\text{m}$ , which has a calculated Pb closure temperature of  $\sim 740\text{ }^{\circ}\text{C}$  at a cooling rate of  $100\text{ }^{\circ}\text{C}/\text{Ma}$ , i.e. slightly higher than that ( $\sim 700\text{ }^{\circ}\text{C}$ ) estimated by Frost et al. (2000), and not very different from that of eudialyte if a  $\sim 50\text{ }^{\circ}\text{C}$  error is considered.

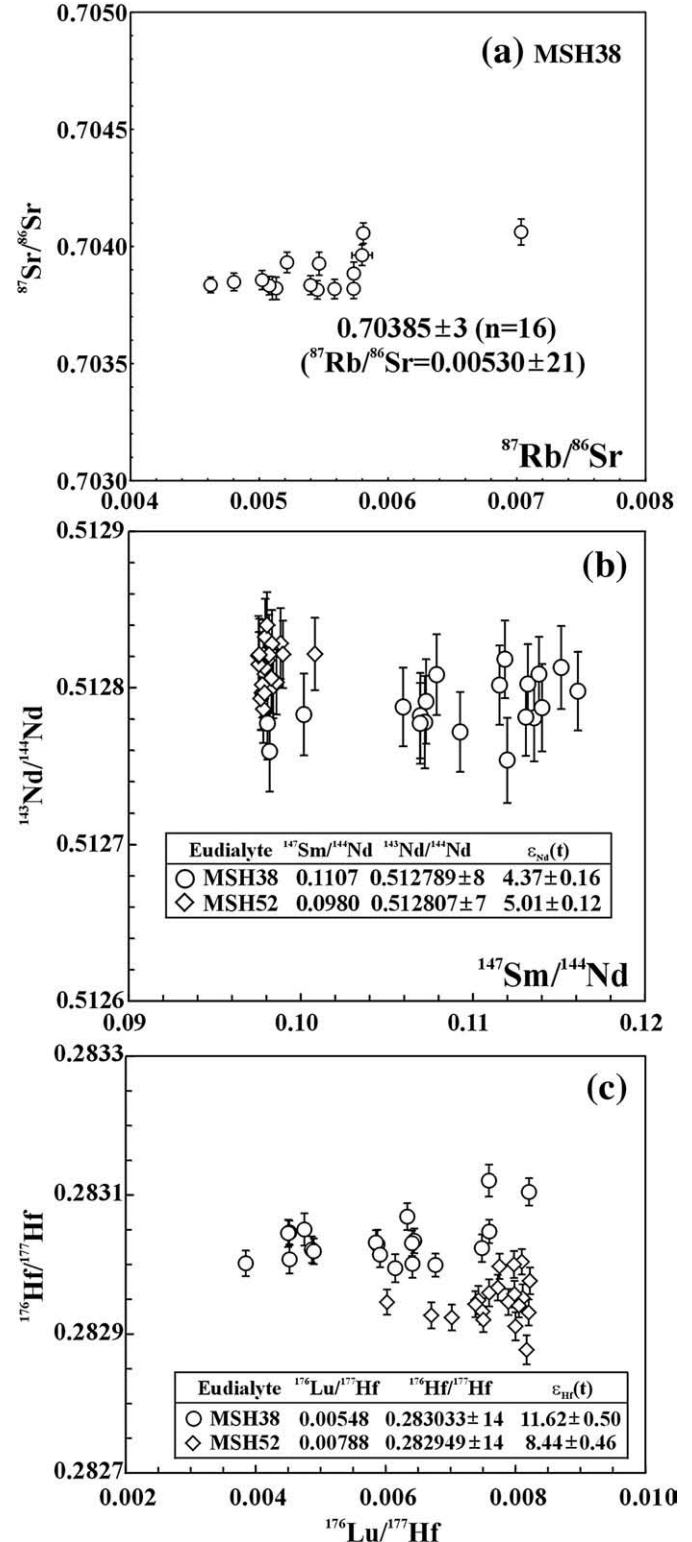


Fig. 11. Sr–Nd–Hf isotopic composition for eudialyte from the Mont Saint Hilaire, Quebec, Canada. (a) Sr isotopic data; (b) Nd isotopic data; and (c) Hf isotopic data.

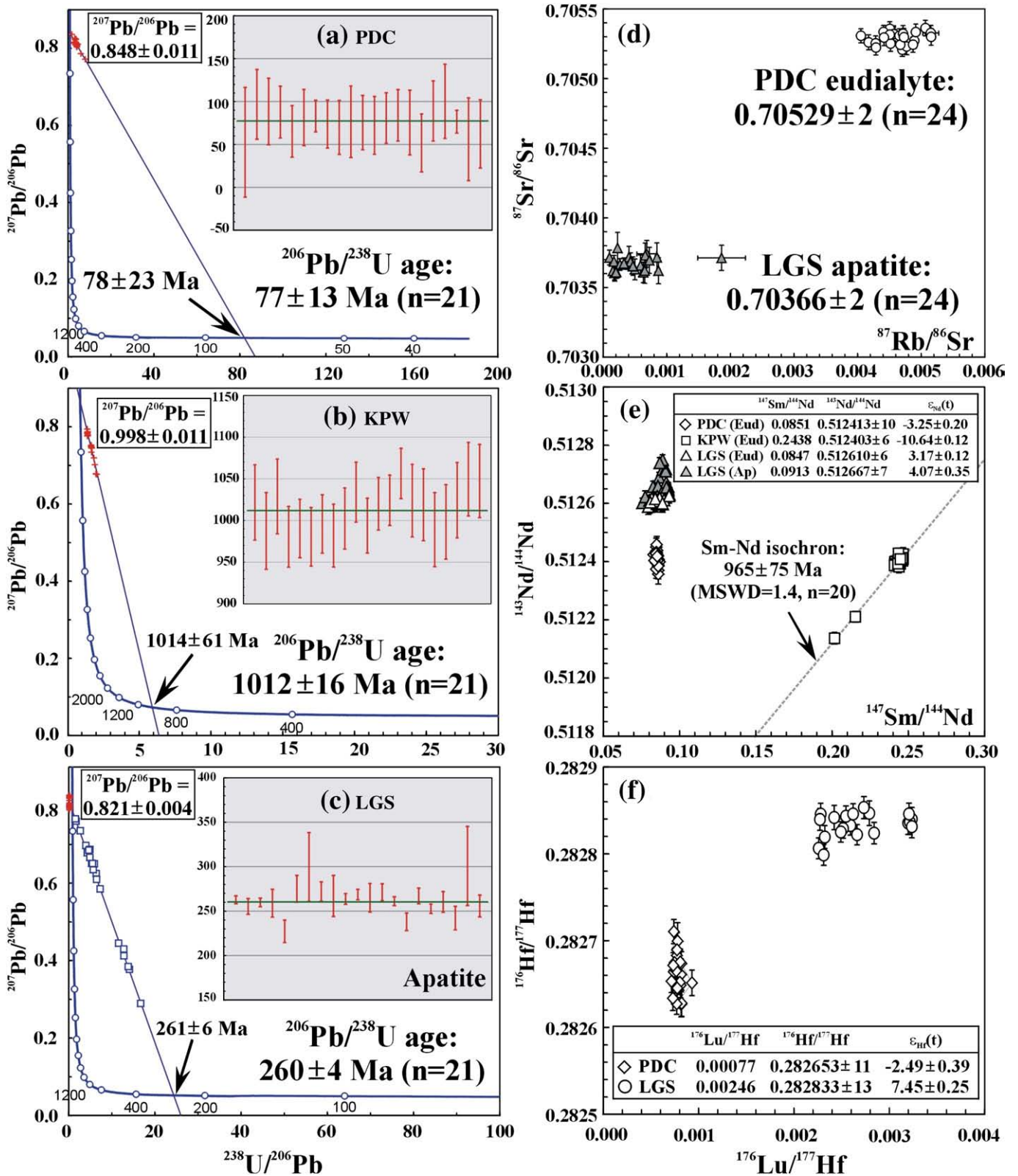


Fig. 12. U–Pb ages, common Pb and Sr–Nd–Hf isotopic composition for eudialyte from the Poços de Caldas (PDC), Brazil, Kipawa (KPW), Quebec, Canada, and Langesund Fjorden (LGS), Norway. (a) PDC (U–Pb); (b) KPW (U–Pb); (c) LGS (U–Pb); (d) Sr isotopic data; (e) Nd isotopic data; and (f) Hf isotopic data.

Finally, we have to consider the composition of common Pb. As shown in this study (Fig. 14b), eudialytes have varying common Pb contents with most ranging from 60 to 100% of the total Pb. This results in the analyses

lying on a chord to Concordia. In such a situation the lower intercept of this discordia line can be considered as the U–Pb age. If there is a datum near the lower intercept, it is possible to obtain a precise age e.g. as shown by



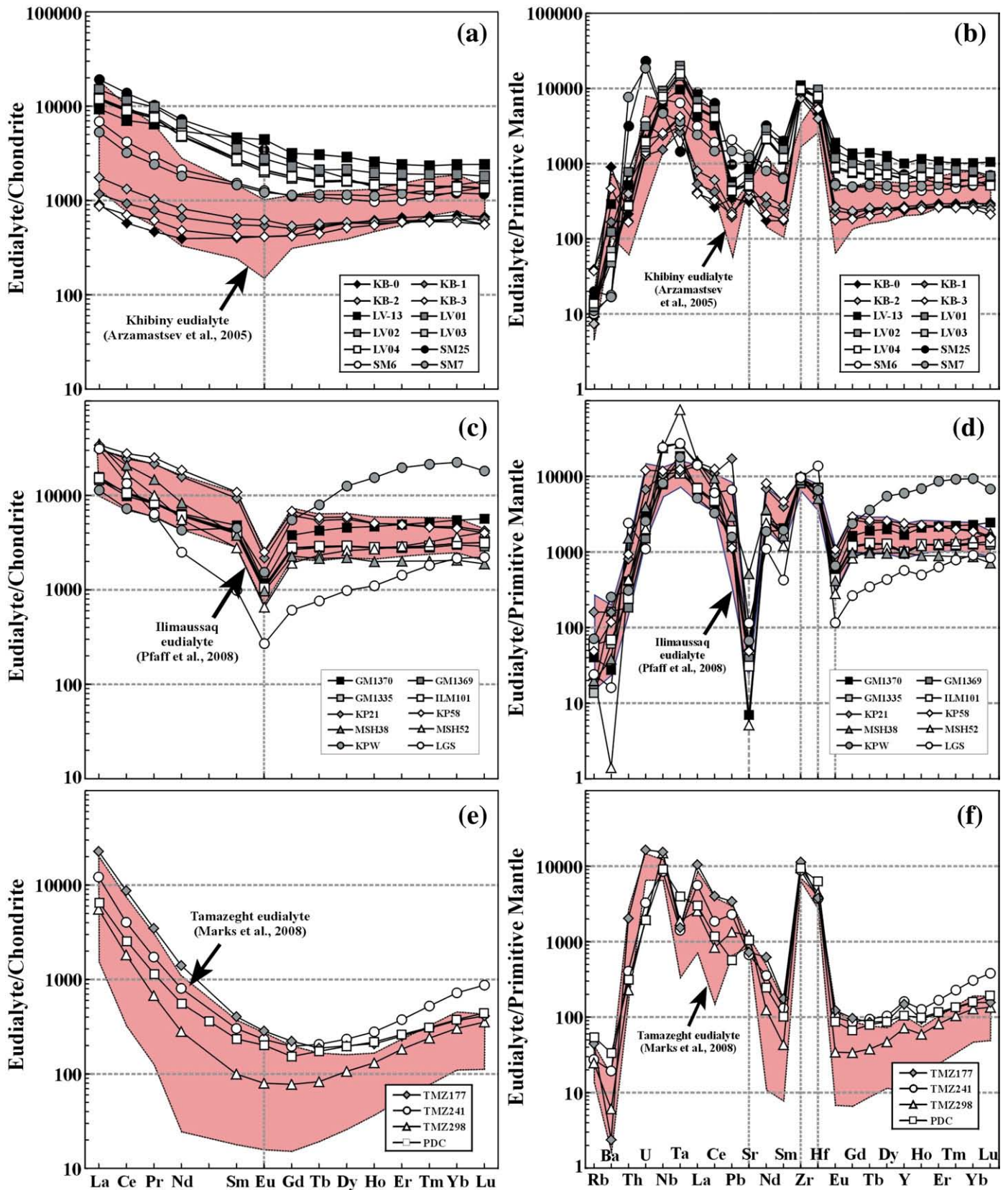


Fig. 13. REE patterns and spidergrams of eudialytes. Three subgroups can be identified, i.e., (a and b) high Sr, (c and d) low Sr and (e and f) low REE. The fields of Khibiny, Ilímaussaq and Tamazeght eudialytes are from Arzamastsev et al. (2005), Pfaff et al. (2008) and Marks et al. (2008b).

sample SM07 (Fig. 8c). Alternatively, a  $^{207}\text{Pb}$  correction is applied to calculate the weighted  $^{206}\text{Pb}/^{238}\text{U}$  age assuming that there has been no Pb loss (Williams, 1998). In this case, the age precision and accuracy depend

on the common Pb composition which is generally determined using the theoretical two-stage model of Stacey and Kramers (1975). Typically this is appropriate for zircon and baddeleyite age determination as their

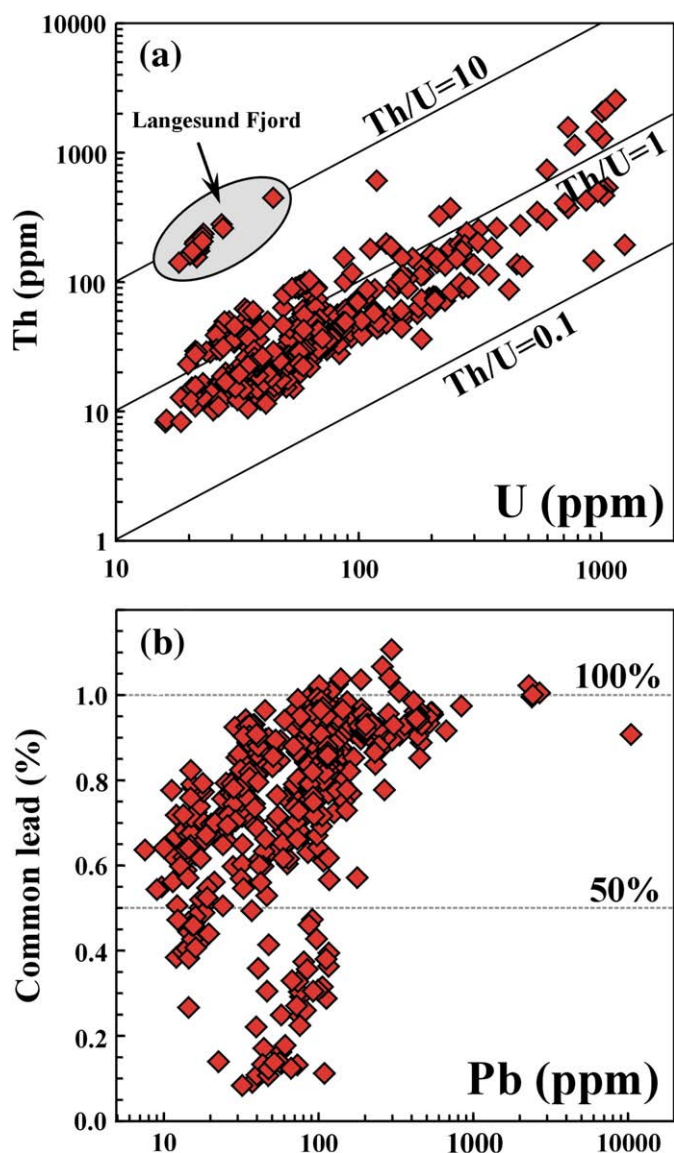


Fig. 14. U, Th and Pb concentrations (a) and percentage of common Pb (b) of eudialytes.

common Pb content is low. In this study, most of our analysed eudialyte data are located in the upper half of the discordia chord and, the two-stage model is not applicable. Therefore, a datum with low common Pb is necessary for determination of the precise composition of common lead. According to the petrographic observations, titanite and apatite always occur in close association with eudialyte, and are considered to have crystallized contemporaneously. Considering that the agpaitic magma generally has a rapid cooling history, and hence the constituting minerals have an identical crystallization age (Markl et al., 2001; Féménias et al., 2005; Krumrei et al., 2006), we suggest, therefore, that titanite and apatite (if present) may be used to construct the above discordia chord. In the sample KB-0, eudialyte defines a discordant chord with a common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of  $0.834 \pm 0.024$  and lower intercept  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $354 \pm 27$  and  $356 \pm 11$  Ma. However, these data combined with those for titanite and apatite, give a common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of  $0.848 \pm 0.011$  and the lower intercept age is  $368 \pm 11$  Ma (Fig. 4a). If this common lead composition is applied, the  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  age for this eudialyte is  $368 \pm 5$  Ma, i.e. more precise than that ( $356 \pm 11$  Ma) obtained by applying the common lead composition as defined by the eudialyte itself (Fig. 4a). With respect to sample SM06, the eudialyte itself yields the lower intercept and  $^{207}\text{Pb}$  corrected  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $217 \pm 39$  and  $220 \pm 15$  Ma. However, if the analyses of eudialyte and titanite are

combined, the ages are identical as  $223 \pm 4$  Ma (Fig. 8a), and more precise than the ages determined from eudialyte alone. Therefore, a datum with low common Pb is vital for obtaining a precise age for eudialyte.

### 5.3. Potential of *in situ* isotopic analysis of eudialyte

Not all minerals can be isotopically measured using *in situ* LA-MC-ICP-MS due to limitations relating to element concentrations and potential interferences. Only those minerals with high concentrations of Sr, Nd and Hf can be used for the determination of Sr, Nd and Hf isotopic compositions with reasonable analytical precision. This limitation raises the question of what elemental concentrations are required for *in situ* Sr, Nd and Hf isotopic ratio determinations that are accurate enough for petrogenetic purposes. With regard to Sr isotopes, two pre-conditions have to be met for highly accurate and precise data; high Sr concentration and low Rb/Sr ratio. The former is necessary for the instrument to yield enough signal intensity, and then high analytical precision, and the latter is needed to avoid interference of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$ . According to our work,  $\sim 500$  ppm of Sr is enough to yield data with a high precision of  $\pm 0.0001$  if a large ( $\sim 140 \mu\text{m}$ ) spot size is used (Fig. 16a). However, a low Rb/Sr ratio is more important than the absolute Sr concentration. In order to evaluate the potential isobaric interference of Rb on Sr isotopes we spiked 200 ppb NBS987 with variable amounts of Rb. The results indicate that samples with Rb/Sr ratios of less than 0.02 ( $^{87}\text{Rb}/^{86}\text{Sr} < 0.05$ ) can be effectively corrected (Yang et al., 2009). In this study, the investigated eudialytes have Rb/Sr ratios from 0.0002 to 0.17 (Fig. 17a), in which some eudialytes from Ilímaussaq (GM1370, KP21, KP58 and ILM101), Mont St. Hilaire (MSH52) and Kipawa (KPW) have Rb/Sr ratios between 0.057 and 0.174; much higher than our Rb/Sr limitation (Table 2). Although three samples (GM1369, GM1335 and LGS) have Rb/Sr ratios lower than our limit, their high HREE concentrations make it impossible to obtain accurate and precise Sr isotopic data. As shown in Fig. 18, Yb/Sr less than 0.1 might be another criterion for *in situ* Sr isotopic analyses of eudialyte. Therefore, not all eudialytes can be analysed by *in situ* laser ablation for their Sr isotopic composition. For suitable samples, the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios calculated from the laser ablation data are consistent with those obtained from solution analysis (Fig. 17b). It is concluded, therefore, that laser ablation of eudialyte can provide reliable Sr isotopic data for petrogenetic purposes.

For Nd isotopic analyses, our previous experiments have shown that the minimum Nd concentration of an ablated subject is approximately 200 ppm using the  $50 \mu\text{m}$  laser spot size (Fig. 16b, Yang et al., 2008). The deviation requirement for practical geological application is  $\pm 2\epsilon$  units, corresponding to a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio deviation of  $+0.0001$ . Considering that our analysed eudialytes have Nd contents of up to 25,624 ppm with most of them above 200 ppm (except TMZ298) (Fig. 17c), it is concluded that Nd isotopic compositions can be precisely measured in all eudialytes. Calculated  $\epsilon_{\text{Nd}}(t)$  values from the ablation data match well with those obtained by solution analyses (Fig. 17d).

Eudialyte is an ideal mineral for *in situ* Hf isotopic analyses. In this study, the eudialytes analysed have Hf concentrations of 719–4708 ppm (Fig. 17e), which are about 5 times less than those of zircon and baddeleyite. Fortunately, we can use a larger spot size to obtain a high signal intensity as the eudialytes analysed are large (mm to cm). For an average Hf concentration of 2000 ppm,  $100\text{--}120 \mu\text{m}$  laser spot size is required if a precision of  $\pm 0.00002$  is expected (Fig. 16c). However, Hf isotopic analysis also requires low Lu and Yb contents for isotopic composition determinations due to interferences from  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$ . Generally, the interference of  $^{176}\text{Lu}$  to  $^{176}\text{Hf}$  is small and can be accurately corrected, as most of our eudialytes have Lu/Hf ratios  $< 0.08$  (which corresponds to  $^{176}\text{Lu}/^{177}\text{Hf} = 0.01$  and  $^{176}\text{Yb}/^{177}\text{Hf} = 0.4\text{--}0.5$ ). The  $^{176}\text{Lu}$  correction on  $^{176}\text{Hf}$  fails in cases such as the KPW eudialyte as its Lu concentration is much higher than other samples with Lu/Hf ratio of 0.2842 (Fig. 17e). Regarding the interference of  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$ , it has been demonstrated that our analytical procedure can be effectively applied to zircons with  $^{176}\text{Yb}/^{177}\text{Hf}$  up to 0.4 (Wu et al., 2006). For sample GM1370

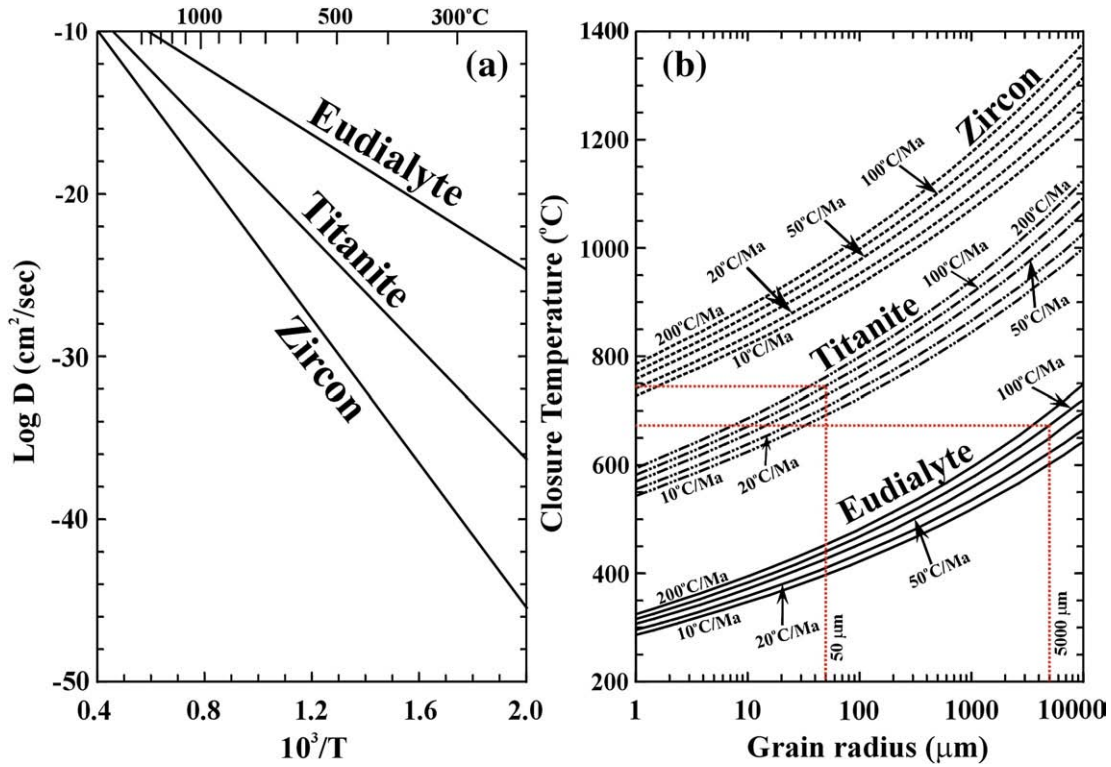


Fig. 15. Theoretical calculation of Pb closure temperature of eudialyte based on the methods of Dodson (1973) and Zhao and Zheng (2007). It is noted that eudialyte has a Pb closure temperature of ~485–695 °C for the grain with size of 1–10 mm at the cooling rates of 10–200 °C/Ma, much lower than that of zircon. However, this temperature is comparable to that of titanite when the latter is one order magnitude smaller of grain-size than eudialyte. The diffusion coefficients of zircon and titanite are from Zhao and Zheng (2007).

(Fig. 3c), which has  $^{176}\text{Yb}/^{177}\text{Hf}$  ratios of 0.236–0.375, the laser analyses yield a  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282337 \pm 15$ , identical to the value of  $0.282318 \pm 5$  obtained by solution method (Table 4). However, for the samples KP21, KP58 and KPW, their  $^{176}\text{Yb}/^{177}\text{Hf}$  ratios exceed 0.4 and range up to 1.8–2.2, making it impossible to obtain accurate Hf isotopic compositions using the *in situ* laser

ablation technique. Except for the sample MSH52, which has Yb/Hf ratio of ~0.4, the calculated  $\varepsilon_{\text{Hf}}(t)$  values from laser ablation data are consistent to those obtained by the solution data (Fig. 17f).

In summary, *in situ* laser ablation can provide accurate and precise Sr, Nd and Hf isotopic data for eudialyte which in most instances are identical to data obtained by our solution analyses (Tables 3 and 4,

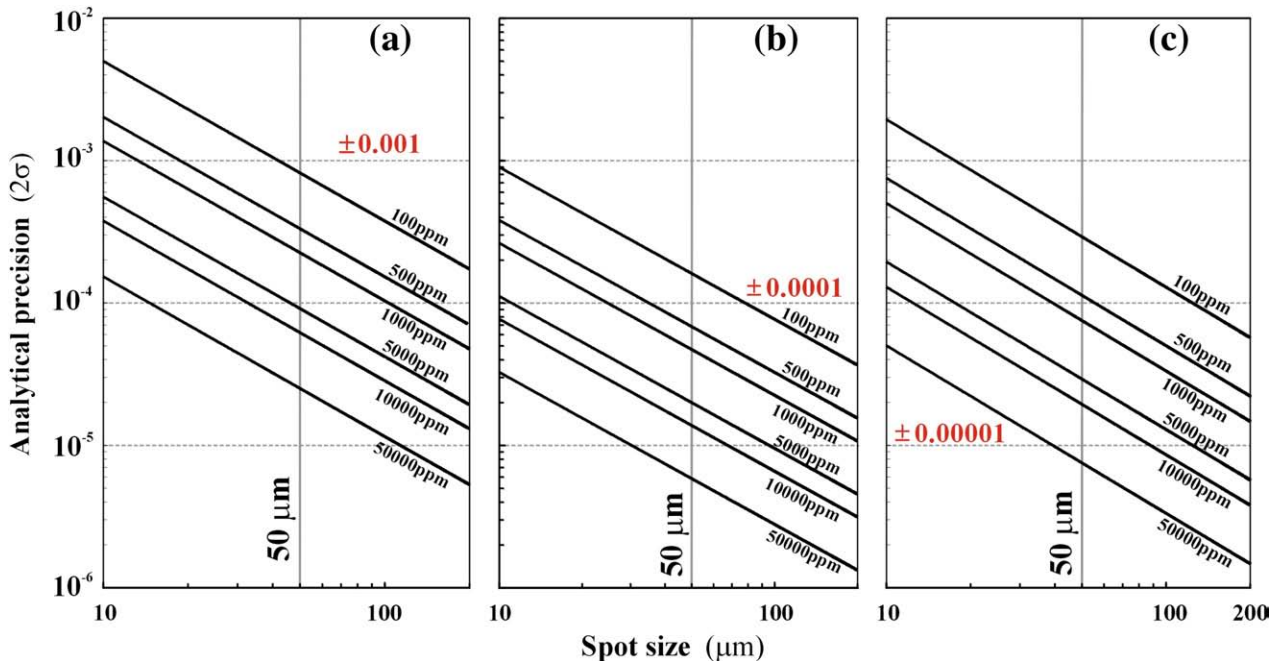


Fig. 16. Relationship between analytical precision of isotopic ratio and spot size during laser ablation analysis. The repetition rate is fixed as 8–10 Hz. (a) Sr isotope, (b) Nd isotope, and (c) Hf isotope.

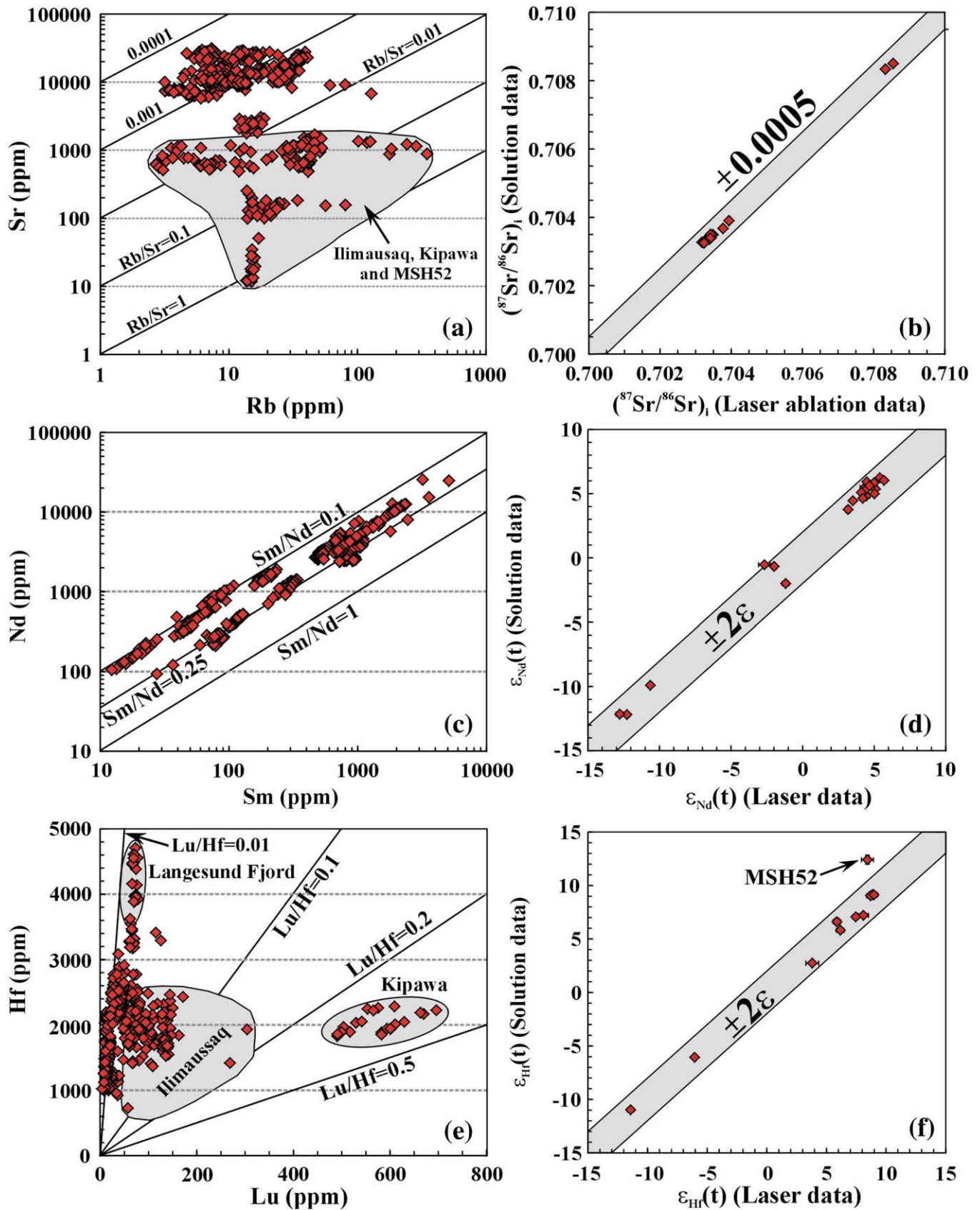


Fig. 17. Elemental variations of Rb–Sr (a), Sm–Nd (b), and Lu–Hf (c) in the eudialytes studied. For suitable samples, the laser ablation results are compared with solution results (b, d and f).

Fig. 17). In our dataset (Table 3), eudialytes from Khibiny, Lovozero, Tamazeght, Mont Saint Hilaire and Langesund Fjord share low  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7034–0.7038) and high  $\epsilon_{\text{Nd}}(t)$  (+3.5 to +5.7) and  $\epsilon_{\text{Hf}}(t)$

(+4.5 to +11.6) values (Tables 3 and 4), indicating derivation from depleted mantle. In contrast, eudialytes from Ilmausaq, Saima, Kipawa and Poços de Caldas show relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$  (>0.705)

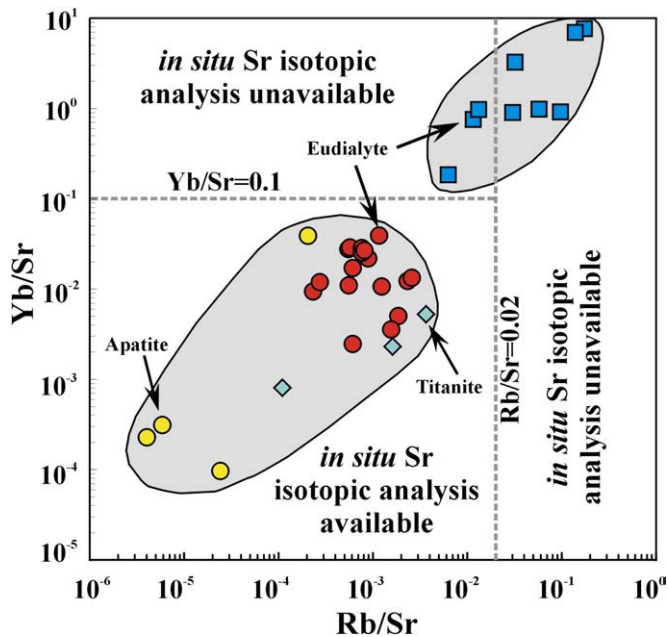


Fig. 18. Rb/Sr and Yb/Sr variation diagram showing possible compositional range for getting accurate Sr isotopic compositions for eudialyte using laser ablation technique.

and low  $\varepsilon_{\text{Nd}}(t)$  (−1.2 to −12.6) and  $\varepsilon_{\text{Hf}}(t)$  (+3.0 to +3.8 for Ilímaussaq, −10.7 to −11.4 for Saima and −3.25 for Poços de Caldas) values, implying derivation from enriched lithospheric mantle and/or contaminated by crustal material during their petrogenesis. Thus, the genesis of apgaitic rocks may involve different mantle sources and suggested that crustal contamination might play a significant role for some of the investigated occurrences.

## 6. Conclusions

Our *in situ* U–Pb, Sr, Nd and Hf analyses of eudialyte lead to the following conclusions:

- 1) Laser ablation can yield reasonable U–Pb ages for eudialyte group minerals as these have high U and Pb contents. However, precise and accurate determination of the common Pb composition is required if an age with high precision and accuracy is expected;
- 2) Eudialyte usually contains high contents of Sr, Nd and Hf coupled with low Rb/Sr and Lu/Hf ratios. Laser ablation can yield accurate Sr, Nd and Hf isotopic compositions with high precision. For eudialyte group minerals with low Sr contents, or high Rb/Sr, Yb/Sr

and Lu/Hf ratios, it is impossible to obtain Sr and Hf isotopic compositions using the laser ablation technique;

- 3) Petrographic observation is always necessary for choosing targets for laser ablation as eudialyte always contains inclusions of earlier-crystallized minerals and is commonly altered. Therefore, *in situ* analysis is an ideal method for age determination and isotopic compositions;
- 4) Analyses of eudialytes from Ilímaussaq, Khibiny, Lovozero, Saima, Tamazeght, Mont Saint Hilaire, Kipawa, Poços de Caldas and Langesund Fjord show a wide range of Sr, Nd and Hf isotopic compositions, indicating that apgaitic rocks are derived from different mantle sources.

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## Appendix A. Sample descriptions

### A.1. Ilímaussaq, Greenland

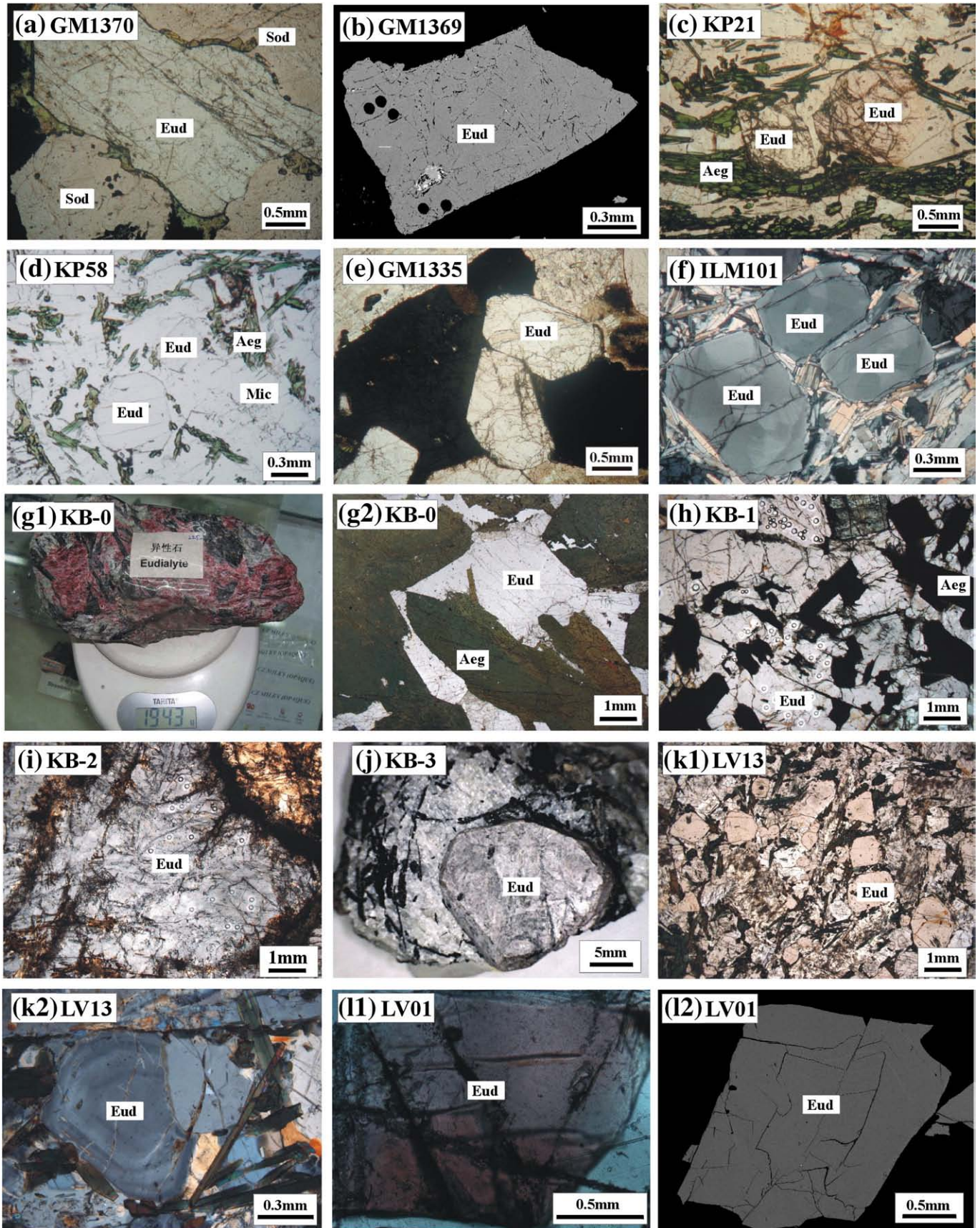
The Ilímaussaq complex, located in southwest Greenland, was emplaced at ~1160 Ma and cooled very rapidly (Waight et al., 2002; Upton et al., 2003; Krumrei et al., 2006). This complex was derived from three magma batches: an early augite syenite; an intermediate alkali granite; and later apgaitic syenites (Marks et al., 2004; Sørensen, 2006). The latter, which form the major part of the complex, are grouped into roof cumulates of sodalite foyaites and naujaites, floor cumulates of kakortokites and residual liquids of lujavrites. According to available data, the Ilímaussaq syenites exhibit a wide Sr–Nd isotopic variation (Blaxland et al., 1976; Paslick et al., 1993; Stevenson et al., 1997; Marks et al., 2004). As far as we are aware, only one sample of Ilímaussaq eudialyte has been analysed for its Hf isotopic composition with  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  values of 0.004595 and  $0.282307 \pm 21$  (Patchett et al., 1981). If the new decay constant of  $^{176}\text{Lu}$  ( $1.87 \times 10^{-9} \text{ y}^{-1}$ ) and updated JMC475  $^{176}\text{Hf}/^{177}\text{Hf}$  value (0.282160) are accepted, the corrected  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $\varepsilon_{\text{Hf}}(t)$  values are  $0.282267 \pm 21$  and  $+4.3 \pm 0.7$ , respectively. In addition, Waight et al. (2002) have reported a high  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio of 0.71149  $\pm 2$  for eudialytes from this complex.

Samples GM1369 (60°58'6.13"N, 45°51'51.96"W, Fig. A1-a) and GM1370 (60°58'2.56"N, 45°52'53.77"W, Fig. A1-b) are naujaite from

Fig. A1. Representative images of eudialytes in the studied samples. (a) GM1370: subhedral eudialyte (Eud), associated with sodalite (Sod), aegirine (green) and arfvedsonite (black); (b) GM1369: BSE image of homogeneous eudialyte (black spots are laser pits); (c) KP21: two eudialyte phenocrysts set in a matrix of aligned aegirine (green), albite and microcline; (d) KP58: euhedral eudialyte associated with microcline (Mic) and needle-like aegirine (Aeg) (after Pfaff et al., 2008); (e) GM1335: euhedral eudialyte associated with interstitial arfvedsonite and K-feldspar (upper left); (f) ILM 101: euhedral, sector-zoned eudialyte crystals set in a fine-grained matrix of euhedral albite laths; (g) KB-0: pegmatitic syenite with purple eudialyte (g1), the eudialyte is subhedral and associated with aegirine (g2); (h) KB-1: subhedral eudialyte and associated aegirine (black); (i) KB-2: subhedral eudialyte with laser pits; (j) KB-3: a euhedral eudialyte crystal within matrix of apatite, aegirine and microcline; (k) LV13: euhedral eudialyte associated with aligned aegirine (dark green), phlogopite (brown) and altered K-feldspar (k1), the eudialyte shows sector zoning; (l) LV01: large eudialyte grain (l1) with homogeneous internal structure (l2); (m) LV02: BSE image of eudialyte (with laser ablation pits); (n) LV03: BSE image of eudialyte (with laser ablation pits); (o) LV04: BSE image of eudialyte (with laser ablation pits); (p) SM06: euhedral eudialytes within a matrix of aegirine, altered nepheline and K-feldspar; (q) SM07: subhedral eudialyte associated with aegirine, altered nepheline, and K-feldspar; (r): SM25 (BSE image): a subhedral eudialyte crystal with marginal alteration; (s) TMZ 177: euhedral eudialytes with inclusions of aegirine needles; (t) TMZ241: subhedral eudialyte set in a matrix of aegirine needles (green) and albite laths; (u) TMZ298: subhedral eudialyte with euhedral inclusion of sodalite, associated with K-feldspar (upper part of the picture) and aegirine (dark green); (v) MSH 38: euhedral eudialyte associated with altered K-feldspar (lower right) and aegirine + arfvedsonite. (w) MSH 52: subhedral eudialyte in a matrix of partly-altered nepheline and K-feldspar associated with euhedral aegirine needles; (x) PDC: BSE image showing aegirine inclusions within eudialyte; and (y) KPW: pegmatitic eudialyte associated with black agrellite (y1). The eudialyte shows homogeneous internal structure in BSE images (y2) (with laser ablation pits); and (z) LGS: large eudialyte phenocryst surrounded by apatite, albite and aegirine (with laser ablation pits).

the roof sequence. They are coarse-grained and consist of sodalite, alkali feldspar, nepheline, amphibole, eudialyte and aegirine. Samples KP21 (60°52′57.35″N, 45°50′17.05″W, Fig. A1-c) and KP58 (60°53′

48.61″N, 45°50′15.10″W, Fig. A1-d) are lujavrite from the middle sequence and consist of aegirine, nepheline, microcline, albite, eudialyte and analcime. Sample GM1335 (60°52′9.61″N, 45°51′



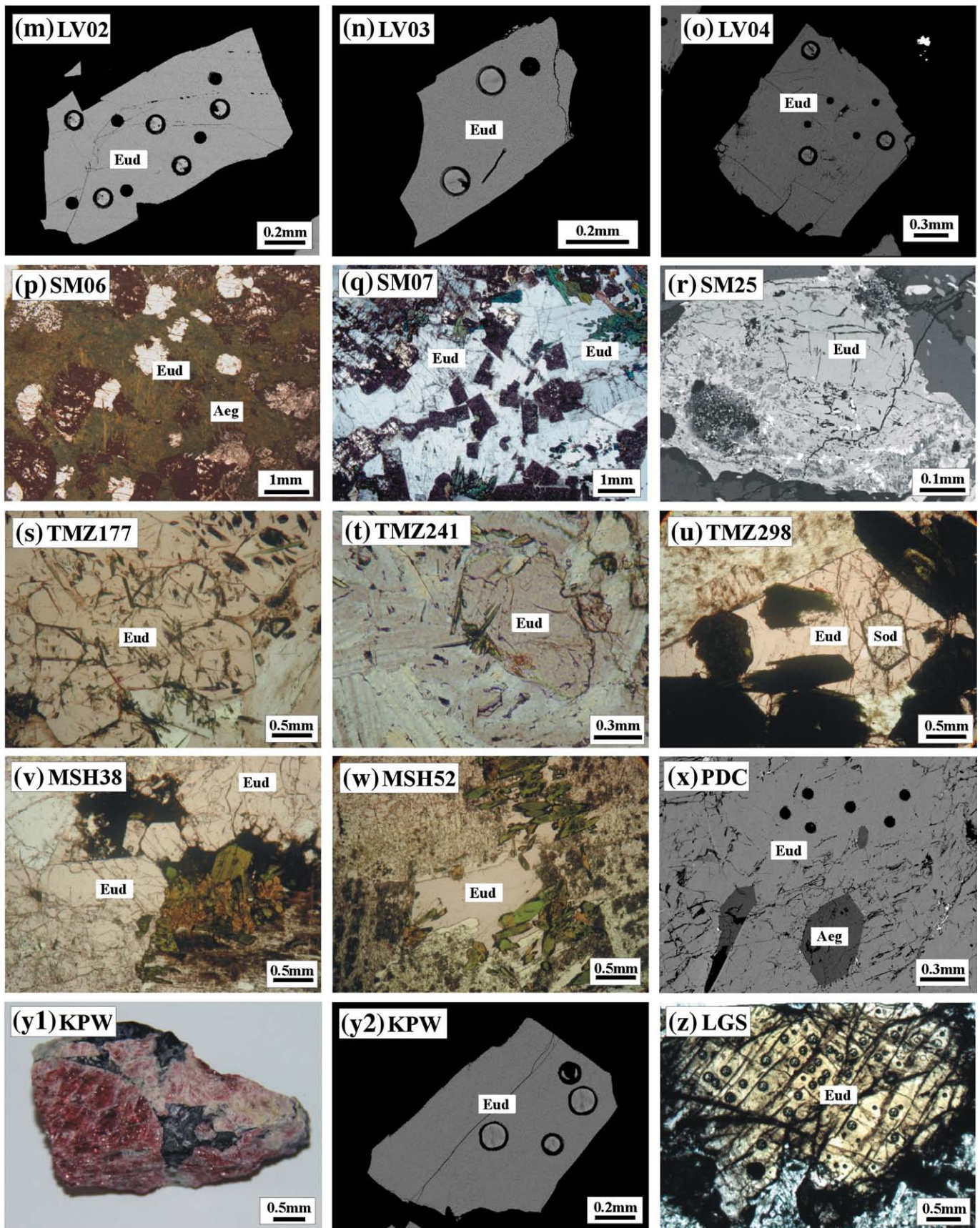


Fig. A1 (continued).

26.05°W) is a kakortkite from the floor sequence, and consists of eudialyte, feldspar, aenigmatite, natrolite and fluorite (Fig. A1-e). Sample ILM101 (60°52′33.27″N, 45°49′11.94″W, Fig. A1-f) is a late dyke of aplite. The detailed mineral compositions and petrology of these samples have been previously described (Markl et al., 2001; 2004, 2007; Pfaff et al., 2008).

#### A.2. Khibiny, Kola, Russia

Khibiny of the Kola Peninsula is the largest alkaline complexes in the world with an area of 1370 km<sup>2</sup> (Arzamastsev et al., 2001). The complex is mainly composed of agpaitic nepheline syenite, ultramafic (peridotite, pyroxenite and melilite-bearing) rocks, and minor carbonatite, in which the nepheline syenite is characterized by extensive occurrence of eudialyte (Arzamastsev et al., 2001, 2005). Available data indicate that this complex was emplaced during the Devonian time with age of ~358 to 388 Ma (Kramm et al., 1993; Kramm and Kogarko, 1994; Downes et al., 2005; Arzamastsev et al., 2007), if the Lu–Hf isochron age of 402.4 ± 2.8 Ma reported by Barfod et al. (2003) is excluded. It was shown that this complex has low initial Sr isotopic ratios of 0.7030–0.7043 with positive  $\varepsilon_{\text{Nd}}(t)$  values of +1.3 to +6.0 (Kramm et al., 1993; Kramm and Kogarko, 1994; Downes et al., 2005). Patchett et al. (1981) reported an <sup>176</sup>Hf/<sup>177</sup>Hf isotopic ratio of 0.282823 ± 18 for one sample of eudialyte from the complex, with <sup>176</sup>Lu/<sup>177</sup>Hf value of 0.00163. If the new decay constant of <sup>176</sup>Lu and updated JMC475 <sup>176</sup>Hf/<sup>177</sup>Hf ratio are accepted, the <sup>176</sup>Hf/<sup>177</sup>Hf and  $\varepsilon_{\text{Hf}}(t)$  values are 0.282783 ± 18 and 8.1 ± 0.6. Using a laser ablation technique, Barfod et al. (2003) obtained <sup>176</sup>Hf/<sup>177</sup>Hf isotopic ratios of 0.282803 ± 7 and 0.282798 ± 15 ( $\varepsilon_{\text{Hf}}(t)$  values of +9.0 ± 0.3 and +8.8 ± 0.5) for the eudialytes in the complex. Similarly, there are three recent studies of Hf isotopic measurements of eudialytes from this complex using laser ablation technique (Korgarko et al., 2008; Lahaye et al., 2008a,b; Kogarko et al., 2010). Although no detailed data are available, it is considered that the Khibiny has an average  $\varepsilon_{\text{Hf}}(t)$  value of +8.0 ± 2.2.

Four samples were selected for analysis in this study. Samples KB-0, KB-1 and KB-2 were collected from the Vostochny open cast mine of Koashva in the Khibiny complex; and KB-3, provided by the Mineralogical Research Company, was collected from the apatite mineral pit at Mt. Rasvumchorr. KB-0 is a massive and laminated nepheline-bearing syenite with a weight of ~2 kg (Fig. A1-g1). It is partly pegmatitic with mineral grain-size of >5 mm. The constituent minerals include: eudialyte (~55%); aegirine (~45%); with minor amounts of aegrellite, titanite, nepheline, albite and potash feldspar, etc. (Fig. A1-g2). Pale pinkish-gray pinacoidal eudialyte occurs as phenocrysts with a diameter of ~20 mm. Sample KB-1 is a coarse-grained nepheline syenite with a mineral assemblage of aegirine; arfvedsonite; nepheline; potash feldspar; and eudialyte (Fig. A1-h). Sample KB-2 is a pegmatite consisting of: aegirine; phlogopite; and eudialyte; with a grain-size of ~1 cm (Fig. A1-i). Sample of KB-3, consists of light greenish apatite, aegirine, microcline and eudialyte, and contains two large pinacoid crystals of eudialyte with grain-sizes of 22 × 22 × 6 and 20 × 18 × 9 mm<sup>3</sup>. The latter crystal was chosen for analyses as it contains few inclusion of aegirine (Fig. A1-j).

#### A.3. Lovozero, Kola, Russia

Lovozero is the second largest alkaline complex in Kola Peninsula with an area of 650 km<sup>2</sup> (Arzamastsev et al., 2001). It is composed mainly of poikilitic feldspathoid syenite, layered lujavrite–foyaite–urtite and eudialyte nepheline syenite (lujavrite) with minor later alkaline volcanic rocks and dykes. Available data indicate that this complex was emplaced during the Devonian time with absolute age of ~347 to 372 Ma (Kramm et al., 1993; Kramm and Kogarko, 1994; Arzamastsev et al., 2007). It was also proposed that this complex had a rapid cooling history (Féménias et al., 2005). Isotopic analyses indicate that this complex is characterized by low initial Sr isotopic

ratios of 0.7034–0.7040 and positive  $\varepsilon_{\text{Nd}}(t)$  values of +2.9 to +4.9 (Kramm et al., 1993; Kramm and Kogarko, 1994; Downes et al., 2005). In recent studies, Hf isotopic measurements of eudialytes from this complex using laser ablation technique yield an average  $\varepsilon_{\text{Hf}}(t)$  value of +6.4 ± 2.3 (Korgarko et al., 2008; Lahaye et al., 2008a,b).

Five samples were collected for this study. Sample LV13 is a coarse-grained melanocratic eudialyte-bearing lujavrite with strong planar lamination (Fig. A1-k1), consisting of alkali feldspar, nepheline, apatite, loparite and eudialyte, in which the euhedral eudialyte develops sector zoning (Fig. A1-k2). Samples LV01 (Fig. A1-l1), LV02 (Fig. A1-l2), LV03 (Fig. A1-m) and LV04 (Fig. A1-n) are large eudialyte crystals from pegmatitic lujavrite in the Alluaiv mining pit.

#### A.4. Saima, China

The ~230 Ma Saima complex is located in the Liaodong Peninsula of northern China. With an area of 280 km<sup>2</sup> (Chen and Saima Deposit Research Group, 1978; Chen, 1996), this complex is composed of an eastern syenite; central alkaline volcanic rocks (trachyte, leucite phonolite and syenitic porphyry); and western nepheline syenite (Jing et al., 1995; Chen, 1996; Zhou et al., 1996). The western coarse-grained eudialyte-bearing nepheline syenite is characterized by uranium mineralization, and consists of nepheline, potassium feldspar; biotite; aegirine; arfvedsonite; aegrellite; eudialyte; and rare rinkolite and lamprophyllite. The eudialyte-enriched syenite typically shows mineral layering with eudialyte comprising up to 90 vol.% locally. The syenite has agpaitic ranging up to 1.5 (Chen, 1996; Tan et al., 1999). Whole-rock analyses give an initial Sr isotopic ratio of ~0.7060–0.7089 (Jing et al., 1995; Chen, 1996; Zhou et al., 1996). No Nd and Hf isotopic data are available for this complex to date.

Three samples (SM06, SM07 and SM25) from the Saima complex were selected for this in this study. These samples have similar mineral assemblages of nepheline, microcline, aegirine, eudialyte, titanite and biotite. Most eudialyte in these samples occur as idiomorphic crystals with grain-sizes up to 1 mm (Fig. A1-p and A1-q). However, some eudialyte from SM25 shows variable degrees of alteration (Fig. A1-r). Rarely, some eudialyte grains occur as pseudomorphs with complete replacement of eudialyte by secondary zircon, catapleite, allanite, aegirine, nepheline, natrolite, titanite.

#### A.5. Tamazeght, Morocco

Tamazeght is a multiple plutonic-to-sub-volcanic complex located in the High Atlas mountains of Morocco, consisting of glimmerite, pyroxenite, shonkinite, gabbro, monzonite and nepheline syenite. The latter form the major component of the complex. The mineral assemblage of the nepheline syenite is nepheline; aegirine; alkali feldspar; eudialyte; titanite; and magnetite (Salvi et al., 2000; Marks et al., 2008a,b). U–Pb age determination of zircons from the monzonite and a late-stage hydrothermal vein yield indistinguishable ages of 44.5 ± 2.2 and 43.1 ± 1.8 Ma, and are taken as the emplacement age of the nepheline syenite (Marks et al., 2008b). The eudialyte samples investigated here are pegmatitic crystals from: a nepheline syenite (TMZ241, 32°31′80.74″N, 4°42′9.56″W, Fig. A1-s)), malignite (TMZ298, 32°31′13.32″N, 4°42′8.38″W, Fig. A1-t); and a late hydrothermal vein within malignite (TMZ177, 32°31′50.56″N, 4°42′55.56″W, Fig. A1-u).

#### A.6. Mont Saint Hilaire, Quebec, Canada

Mont Saint Hilaire is part of the east–west trending Cretaceous anorogenic igneous Monteregian province of Quebec, which includes the Oka carbonatite. Mont Saint Hilaire is a mafic–alkaline intrusion composed of pyroxenite; gabbro; monzonite; and nepheline syenite (Currie et al., 1986). A peralkaline syenite, characterized by a negative Eu anomaly forms the eastern part of the complex together with phonolite. Three analyses of whole-rock samples gave initial Sr isotopic values of 0.7037–0.7051



(Currie et al., 1986). Sample MSH38 (45°33'37.41" N, 73° 8'28.53"W, Fig. A1-v) and MSH52 (45°33'38.30"N, 73° 8'29.33"W, Fig. A1-w) in this study are coarse-grained (~5 mm) eudialytes from the nepheline syenite consisting of aegirine; Na-rich amphibole; nepheline; sodalite; ilmenite; magnetite, and eudialyte.

#### A.7. Poços de Caldas, Brazil

Poços de Caldas is the largest alkaline complex in South America with an area of ~800 km<sup>2</sup> (Schorscher and Shea, 1992), and is composed of peralkaline phonolite and nepheline syenite. The complex is subdivided into eudialyte-bearing and eudialyte-free syenites. It is generally accepted that the eudialyte-free nepheline syenite was formed at ~78 Ma, with initial Sr isotopic ratio of ~0.7051 and  $\epsilon_{\text{Nd}}(t)$  value of ~-3.5 (Shea, 1992). No previous data are available for the eudialyte-bearing nepheline syenites. Sample PDC, kindly provided by Michele Lustrino, was collected from the outcrop of Pedra Balao, a typical location for eudialyte in the north of the complex. The mineral is associated with nepheline; potassium feldspar; aegirine. The analysed eudialyte is pink in colour with grain-size of ~10 mm (Fig. A1-x).

#### A.8. Kipawa, Quebec, Canada

The sample KPW was collected from the Kipawa complex located in the Grenville province in Quebec of Canada. This complex, of nepheline syenite, amphibole syenite, quartz syenite and alkali granite, lies within gneiss as sheet-like body along the boundary between granitic and metasedimentary rocks (Currie and van Breemen, 1996). Geochronology suggests that the complex was emplaced ~1030 Ma ago, and underwent later metamorphism or genetically related to alkaline metasomatism from 1035 to 990 Ma (Currie and van Breemen, 1996; van Breemen and Currie, 2004). The eudialyte in this complex occurs in the late agpaite pegmatites (Edgar and Black, 1972; Fryer and Edgar, 1977). The analysed sample is a mass of rose pink eudialyte with very minor dark purple veinlets of fluorite and minor aegirine. Eudialyte in this sample ranges from ~1 to 30 mm (Fig. A1-y).

#### A.9. Langesund Fjord, Norway

Langesunds Fjord is one of the well-known locations of eudialyte, which was traditionally named as euclite (Bollinger et al., 1983). The sample LGS is a medium-grained nepheline syenite collected at Arøy in Langesund Fjord, southeast of the Larvik complex; the latter being a part of the Permian Oslo alkaline province (Neuman, 1980). The eudialyte, occurred as phenocryst with grain-size of 1–5 mm, is associated with nepheline, aegirine, potassium feldspar, albite and apatite (Fig. A1-z).

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