

**Quantitative extraction of noble gases by in vacuo crushing:
Implications for Ar-Ar dating and measurement of scapolite
Br/Cl and I/Cl**

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1. Introduction

In vacuo crushing is commonly employed to release noble gases from fluid inclusions and vesicles. In addition, it has gained some application in the determination of Ar-Ar ages for ore-related and metamorphic minerals (e.g. (Qiu, 1996; Qiu and Jiang, 2007; Qiu and Wijbrans, 2006). However, one of the most recent of these ‘in vacuo crushing’ Ar-Ar ages has proven controversial (Kendrick, 2007; Qiu and Wijbrans, 2006; Qiu and Wijbrans, 2007; Zhao and Gao, 2007). Importantly, the interpretation of this age depends critically on the source of Ar isotopes released during *in vacuo* crushing, and the age could be an artifact if *in vacuo* crushing releases significant noble gases from mineral impurities in the matrix (Kendrick, 2007).

Scapolite is a metamorphic mineral with extremely variable composition: $\{(Ca,Na,K)_4Al_3(Al,Si)_3O_{24}(CO_3,SO_4,OH,Cl)\}$. Scapolite is of interest because it records the volatile content of metamorphic fluids, including their XCO_2 , fSO_4 and salinity (Kullerud and Erambert, 1999; Markl et al., 1998; Markl and Piazzolo, 1998; Mora and Valley, 1989). Extended Ar-Ar methodology (Irwin and Reynolds, 1995; Kendrick et al., 2006b; Turner, 1965) could be used to simultaneously investigate the halogen (Cl, Br and I) composition of scapolite and further test its suitability for Ar-Ar dating (Reddy et al., 1997). However, the high volatile content of scapolite means that it is not suited to stepped heating analysis.

In this contribution we test *in vacuo* crushing as a mechanism to release irradiation-produced potassium and halogen-derived noble gas isotopes ($^{39}Ar_K$, $^{38}Ar_{Cl}$, $^{80}Kr_{Br}$ and $^{128}Xe_I$) from the scapolite mineral lattice. Independent measurement of Cl and K by the electron microprobe, and comparison with noble gas release spectra from fluid inclusion bearing quartz, confirm that some prolonged *in vacuo* crushing procedures release noble gases from mineral lattices quantitatively (Kendrick, 2007).

This has important implications for understanding Ar-Ar ages obtained by *in vacuo* crushing (Qiu, 1996; Qiu and Jiang, 2007; Qiu and Wijbrans, 2006), measurement of noble gas initial ratios in fluid inclusions (e.g. (Kendrick et al., 2008), and confirms that extended Ar-Ar methodology together with *in vacuo* crushing can be used to investigate scapolite Br/Cl and I/Cl compositions.

2. Samples and methods

The samples selected include a scapolite gem from Hunza, Pakistan (SP; Fig 1a) and three scapolites from localities in the 1.1 Ga Grenville Province of Canada, at Tory Hill, Bancroft, Ontario (TB-O), Bear Lake, Quebec (BL-Q) and the Lawrence-McGill Farm, Quebec (LM-Q). The scapolites were all analysed by microscopy; fluid inclusions are virtually absent in the gem sample (Fig 1bc) and have a very low abundance in the Grenvillian samples. Electron microprobe analysis indicates SP has a Cl-rich marialitic composition with 3.4 wt % Cl and 1.1 wt % K₂O. Samples TB-O and BL-O have 1.47 and 1.67 wt % Cl and 0.87 and 0.94 wt % K₂O. Sample LM-Q has a Cl-poor meionitic composition with just 0.01 wt % Cl and a molar K/Cl of ~21 (Table 1). The scarcity of fluid inclusions means that the scapolite matrix is the main reservoir of both Cl and K in these samples. However, fluid inclusions could have minor significance as a Cl reservoir in the LM-Q sample with the lowest matrix concentration of Cl (Table 1). As a contrast to the scapolite, a piece of hydrothermal quartz was chosen from the Mt Isa Inlier, with abundant fluid inclusions (Fig 1d). Fluid inclusions are the only significant reservoir of Cl in hydrothermal quartz (Kendrick et al., 2006b).

The samples were crushed and 1-2 mm sized grains hand picked under a binocular microscope. Mineral grains were washed in an ultrasonic bath using

distilled water and acetone and packed in Al-foil packets. The packets were loaded into a silica glass tube with Ar-Ar flux monitors (Hb3Gr, GA1550), the shallowwater I-Xe standard (Hohenberg 1967; Roddick 1983; McDougal and Harrison 1999; Johnson et al. 2000), pure CaF₂ and K-glass. The package was irradiated for 150 Megawatt hours in position 5c of the McMaster nuclear reactor, Canada (Irradiation designated UM#17). The irradiation parameters (Kelley et al. 1986) were determined as: $J = 0.0157$; $\alpha = 0.84$; and $\beta = 5$; indicating a combined fast and thermal neutron fluence of approximately $10^{19} \text{ n cm}^{-2}$. The resonant neutron correction factors were 1.17 for Br and 1.47 for I (Kendrick et al. 2006a).

Irradiated samples (5-20 mg) were loaded into the air-actuated *in vacuo* crushing device (Matsumoto et al., 2001) and 200-2500 crushes progressively pulverised each sample in steps of 20 minute duration. Duplicate analyses were undertaken with 5-50 mg of selected samples using modified Nupro® valves. Extracted gas was purified using hot and cold Zr-Al getters and expanded into the MAP-215 noble gas mass spectrometer at the University of Melbourne. Isotopes of Ar, Kr and Xe were simultaneously analysed in peak jumping mode in 9 cycles of measurement over a period of 50 minutes. Argon was measured on the Faraday detector while the less abundant isotopes of Kr and Xe were measured on a Johnson electron multiplier at a relative gain of ~400.

Machine blanks were monitored throughout the period of analysis. An atmospheric blank was significant in the air-actuated *in vacuo* crushing device, but the blank for K or halogen-derived noble gases was beneath the detection limit for both the air-actuated and nupro crushing devices. Cl, K, Ca, Br and I were determined from the neutron flux and the measured abundance of irradiation-produced nucleogenic noble gas isotopes: ³⁸Ar_{Cl}, ³⁹Ar_K, ³⁷Ar_{Ca}, ⁸⁰Kr_{Br} and ¹²⁸Xe_I. Standard

corrections were made for post irradiation decay of ^{37}Ar and ^{36}Cl (producing ^{36}Ar) and for other Ar interference reactions. The Br/Cl and I/Cl values are proportional to the measured $^{80}\text{Kr}_{\text{Br}}/^{38}\text{Ar}_{\text{Cl}}$ and $^{128}\text{Xe}_{\text{I}}/^{38}\text{Ar}_{\text{Cl}}$ values and analytical precision is better than 3%. However, based on analysis of the shallowwater standard and the reproducibility of Br/Cl values in several irradiations, the total 1σ uncertainty is estimated as $\sim 10\%$ for Br/Cl and I/Cl in this irradiation (Kendrick et al. 2006a).

3. Results and discussion

3.1 Scapolite release spectra

Considerable quantities of halogen-derived noble gas were released from the scapolite lattice during *in vacuo* crushing (Table 2). A 7.3 mg aliquot of sample SP was studied by air-actuated *in vacuo* crushing in detail. The gradual release of lattice-derived noble gas from this sample, is displayed graphically, and contrasted with the rapid release of noble gas from fluid inclusions in quartz, in Figure 2.

The first extraction step of 1000 crushing strokes released 0.02 volts of $^{38}\text{Ar}_{\text{Cl}}$ on the Faraday detector, equivalent to 1.3 % of the total $^{38}\text{Ar}_{\text{Cl}}$ released by this sample (Appendix). The number of crushing strokes was increased to 2500 per extraction, yielding a maximum $^{38}\text{Ar}_{\text{Cl}}$ signal of 0.085 volts in the nineteenth step. Subsequently, a gradually diminishing quantity of $^{38}\text{Ar}_{\text{Cl}}$ was released per extraction, giving a signal approximately ten times less than the maximum value after 96,000 crushing strokes (Fig 2).

The total amount of $^{38}\text{Ar}_{\text{Cl}}$ released during the entire crushing experiment was equivalent to 7.6×10^{-6} mols of Cl, representing 3.53 wt % of the 7.3 mg sample. The Cl concentration inferred from the release of $^{38}\text{Ar}_{\text{Cl}}$ by *in vacuo* crushing is within uncertainty of the Cl concentration (3.41 ± 0.07 wt %) determined by the electron

microprobe (Table 1). This indicates that prolonged *in vacuo* crushing can quantitatively remove noble gases from a mineral matrix and the decreasing rate of noble gas extraction during the experiment is attributed to their gradual removal from the scapolite lattice (Fig 2).

3.1.1 Mechanism of noble gas release and fractionation

The two most plausible mechanisms by which *in vacuo* crushing could release noble gases from the scapolite matrix are: i) thermal diffusion enabled by heat generated during repeated crushing of the sample, and ii) mechanical disaggregation of the scapolite lattice. Thermal diffusion is rejected because attempts to analyse scapolite by stepped heating released less than 0.001% of $^{38}\text{Ar}_{\text{Cl}}$ at temperatures of 400 °C, and significant outgassing only occurred at temperatures of 1000-1200 °C when scapolite broke down and then melted. This means *in vacuo* crushing is advantageous for the analysis of volatile bearing mineral phases. The minerals are broken down mechanically, not chemically, and so volatiles such as carbonate are not released as CO_2 (cf. stepped heating).

The *in vacuo* crushing extraction profiles are similar for ^{38}Ar , ^{80}Kr and ^{128}Xe (Fig 2). However, the rate of $^{38}\text{Ar}_{\text{Cl}}$ extraction decreases quicker than the rate of $^{80}\text{Kr}_{\text{Br}}$ or $^{128}\text{Xe}_{\text{I}}$ extraction: the normalized $^{38}\text{Ar}_{\text{Cl}}$ release in the final extraction step was just 10% of the maximum value, compared to 12% for $^{80}\text{Kr}_{\text{Br}}$ and 19% for $^{128}\text{Xe}_{\text{I}}$ (see Fig 2; Appendix). The relative change in the amounts of $^{38}\text{Ar}_{\text{Cl}}$, $^{80}\text{Kr}_{\text{Br}}$ and $^{128}\text{Xe}_{\text{I}}$ released in each extraction step results in a systematic ‘apparent’ change in the measured Br/Cl and I/Cl values throughout the experiment (Fig 3).

The fractionation effect maybe explained because the heavier noble gases are more strongly adsorbed onto the crushed sample than the lighter noble gases. As a

result light noble gases are preferentially released ($^{38}\text{Ar}_{\text{Cl}} > ^{80}\text{Kr}_{\text{Br}} > ^{128}\text{Xe}_{\text{I}}$) in the early part of the experiment resulting in low Br/Cl and I/Cl values. As the sample becomes depleted in $^{38}\text{Ar}_{\text{Cl}}$ relative to $^{80}\text{Kr}_{\text{Br}}$ and $^{128}\text{Xe}_{\text{I}}$, artificially high Br/Cl and I/Cl values are obtained in the final extraction steps (Fig 3). This implies that the mean Br/Cl and I/Cl values determined for the sample are most representative of the samples true Br/Cl and I/Cl values.

The non-systematic variation in the K/Cl value, cannot be explained by adsorbtion phenomena, because the isotopes of Ar have similar adsorbtion characteristics. Therefore, the variation in K/Cl (Fig 3) could indicate that there is some compositional variation within the scapolite and that noble gases are released from different reservoirs within the scapolite as crushing progresses. Ar-Ar ages, which also depend only on the measurement of Ar-isotopes only will also be unaffected by the adsorbtion effect.

3.1.2 Implications for Br/Cl and I/Cl measurement

The geological significance of Br/Cl and I/Cl values determined for SP and other scapolites will be explored elsewhere. The aim of this contribution is to document the noble gas release mechanism and its implications for Br/Cl, I/Cl and Ar-Ar age measurement. Despite the fractionation in Br/Cl and I/Cl identified above, *in vacuo* crushing represents a suitable technique for Br/Cl and I/Cl analysis because the first ten extraction steps have reproducible compositions (Fig 3). In addition, the Br/Cl and I/Cl values determined in these steps are only slightly lower than the sample mean (true) value (Fig 3), and the difference in the measured and true values is insignificant compared to the 10% uncertainty in Br/Cl resonant neutron correction factor (for this irradiation) and the orders of magnitude variation in Br/Cl and I/Cl values determined

for crustal fluids (e.g. (Hanor, 1994; Kendrick et al., 2006a; Kendrick et al., 2007; Worden, 1996).

3.2 Scapolite (in vacuo crushing) Ar-Ar ages

The samples gave variable results for Ar-Ar dating,. Sample SP studied in the most detail (above) contained very little K or radiogenic $^{40}\text{Ar}^*$, with atmospheric ^{40}Ar accounting for 90-100% of the total ^{40}Ar released in approximately half of the extraction steps (Appendix). The Grenvillian samples contained a higher proportion of radiogenic $^{40}\text{Ar}^*$ equal to more than 70-90% of the total ^{40}Ar in the majority of extraction steps. The data from these samples is plotted on age plateau diagrams in Figure 4.

The westernmost sample from the Bancroft Domain in Ontario (TB-O) was subjected to 8 extraction steps comprising 10,000 crushing strokes. The total amount of $^{38}\text{Ar}_{\text{Cl}}$ and $^{39}\text{Ar}_{\text{K}}$ released during the course of this experiment was equivalent to Cl and K concentrations of 0.09 and 0.03 wt %, respectively. These values are considerably lower than those determined by electron microprobe (Table 1), suggesting less than 6% of the total noble gases were released. Of the ^{39}Ar released from this sample, 71% of it defined a plateau age of ~1006 Ma, and it is only the first and last extraction steps that are discordant (Fig 4).

Samples BL-Q and LM-Q were each subjected to 15 extraction steps comprising 31,500 and 28,700 crushing strokes, respectively. The total amount of $^{38}\text{Ar}_{\text{Cl}}$ and $^{39}\text{Ar}_{\text{K}}$ released from BL-Q was equivalent to Cl and K concentrations of 0.6 and 0.7 wt % respectively. These values are lower than those determined by electron microprobe (Table 1) suggesting 38 to 70% of the total noble gases were released

from this sample. Of the ^{39}Ar released 91% of it defined a plateau age of ~ 731 Ma and only the first extraction step was discordant (Fig 4).

The total amount of $^{38}\text{Ar}_{\text{Cl}}$ and $^{39}\text{Ar}_{\text{K}}$ released from LM-Q was equivalent to Cl and K concentrations of 0.01 and 1.7 wt % respectively. The Cl concentration is comparable, but the K concentration is much greater, than that determined by electron microprobe (Table 1). The reason for this discrepancy is unclear, however, as the volume of $^{39}\text{Ar}_{\text{K}}$ and $^{38}\text{Ar}_{\text{Cl}}$ was similar in each extraction step the sample was incompletely outgassed, suggesting the real K and Cl concentrations are much greater than measured. Of the ^{39}Ar released from this sample 95% of it defines a plateau age of ~ 370 Ma and only the first extraction step is discordant (Fig 4).

The apparent Ar-Ar ages obtained by *in vacuo* crushing scapolite represent the apparent age of the scapolite lattice, not fluid inclusions (cf (Qiu and Wijbrans, 2006)). The mechanical release of the noble gases by disaggregation of the scapolite lattice, means that *in vacuo* crushing Ar-Ar ages are similar to Ar-Ar ages obtained for hydrous minerals, that breakdown during stepped heating: the spectra cannot be related to thermal diffusion. However, the spectra do provide more information than K-Ar or total fusion Ar-Ar ages. For example, a minor Ar contribution from the rare fluid inclusions present in these samples could account for the discordant first step of the experiments (Fig 4).

3.2.1 Regional context and significance of the ages

Scapolitisation in the Grenville Province was related to hydrothermal activity associated with three episodes of anorthosite-mangerite-charnokite-granite magmatism and metamorphism between ~ 1.2 and 1.0 Ga (Higgins and Breeman,

1996). The oldest scapolite apparent age of 1006 ± 24 determined for sample TB-O from the Bancroft Domain of the Central Metasedimentary Belt (Fig 5), is within error of the youngest phase of magmatism between 1010-1020 Ma (Higgins and Breeman, 1996). This age is also similar to Ar-Ar metamorphic cooling ages obtained for hornblende from the Bancroft and Elzevir Domains of the Central Metasedimentary Belt (Cosca et al., 1992; Cosca et al., 1991). The hornblende Ar-Ar ages show a discontinuous increase across the Central Metasedimentary Belt toward the east (Fig 5), suggesting uplift and exhumation occurred differentially across the province (Cosca et al., 1992).

The much younger apparent age of 731 Ma determined for scapolite BL-Q to the north-east is similar to Ar-Ar 'plateau' ages obtained for K-feldspar from the Elsevir and Frontenac Domains in the Central Metasedimentary Belt (Fig 5; (Streepey et al., 2002). The youngest apparent age of 370 Ma determined for scapolite LM-Q, also in Quebec, is younger than any 'plateau' ages determined for feldspar, but is similar to the lowest age steps obtained for feldspars from the Elsevir and Frontenac Domains mention previously (Streepey et al., 2002). This age is only slightly older than the Carboniferous Alleghenian Orogeny that effected the northern Appalachians southeast of the Grenville Province (Fig 5).

The spectrum of ages obtained for Grenvillian scapolite suggest widely different Ar retentivities for scapolite. The ~ 1 Ga age obtained for TB-O suggests that under the right circumstances scapolite is retentive to Ar. However, the youngest age of 370 Ma obtained for LM-Q suggests scapolite can be even more susceptible to Ar-loss than K-feldspar. These contradictory behaviours could be related to variations in the thermal regime across the Grenville Province during the Phanerozoic (Cosca et al., 1992; Streepey et al., 2002). If this is the case it is further suggested that

the eastern most part of the province was affected by very mild Alleghenian deformation. However, an alternative explanation is that the Ar retentivity of scapolite is strongly dependent on the composition of scapolite. Possibly indicating that CO₂-rich meionitic scapolite is more susceptible to Ar-loss than marialitic scapolite (Table 1 and Fig 4).

4. Summary and Implications

Detailed *in vacuo* crushing studies of scapolite and quartz demonstrate that matrix hosted noble gases can be quantitatively released by prolonged *in vacuo* crushing (Fig 2).

- This confirms that published ‘*in vacuo* crushing’ Ar-Ar ages could be related to mineral impurities within the K-poor samples selected, and not the fluid inclusions; as suggested by (Kendrick, 2007) (cf. (Qiu, 1996; Qiu and Wijbrans, 2006; Qiu and Wijbrans, 2007)).
- Prolonged *in vacuo* crushing combined with Ar-Ar methodology has been demonstrated as a viable technique for investigation of scapolite Br/Cl and I/Cl values. A fluid inclusion contribution can be recognised if the first step(s) are discordant, and the Br/Cl and I/Cl values obtained in the first ten extraction steps are reproducible and within error of the true values (Fig 3).
- The slow release of matrix-hosted noble gases confirms that *in vacuo* crushing can be used to selectively analyse fluid inclusions. 1000 crushing strokes released only 1.3 % of the matrix noble gases from scapolite (SP), whereas 1100 crushing strokes released ~70% of the noble gas hosted by fluid inclusions in quartz (Fig 2). Therefore, the matrix noble gas component will

be negligible in fluid inclusion rich samples subjected to a fewer than ~1000 crushing strokes.

- Scapolite has been shown to have some potential as an Ar-Ar geochronometer, but further work is required to understand the factors controlling its retentivity to Ar isotopes.
- Air-actuated *in vacuo* crushing, and similar *in vacuo* crushing procedures, could have application for Ar-Ar dating (or Br/Cl and I/Cl determination) of other volatile rich minerals (e.g. tourmaline) that contain minor K or Cl and are not well suited to stepped heating experiments.

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Table 1. Electron microprobe analyses of scapolite minerals

	<u>Gem</u>		<u>Grenville Province</u>					
	<u>SP</u>		<u>TB-O</u>		<u>BL-Q</u>		<u>LM-Q</u>	
SiO₂	60.9	0.9	50.4	0.2	50.9	0.7	43.9	0.1
TiO₂	0.01	0.01	0.01	0.01			0.02	0.02
Al₂O₃	18.9	0.2	24.0	0.1	23.6	0.3	28.0	0.1
FeO	0.04	0.01	0.06	0.02	0.06	0.02	0.004	0.003
MgO			0.015	0.001	0.011	0.008	0.019	0.007
CaO	1.8	0.1	11.8	0.1	11.0	0.2	18.4	0.7
Na₂O	12.5	0.1	6.3	0.2	6.7	0.1	2.8	0.4
K₂O	1.10	0.05	0.87	0.04	0.94	0.04	0.42	0.09
SO₃	0.13	0.05	1.17	0.04	0.99	0.02	1.22	0.20
Cl	3.41	0.07	1.47	0.06	1.67	0.03	0.01	0.20
CO₂¹	0.78	0.06	2.33	0.06	2.19	0.04	3.99	0.13
.-Cl=0	0.77	0.01	0.33	0.01	0.38	0.01	0.00	0.04
TOTAL	98.9	0.7	98.2	1.1	97.8	0.2	98.8	0.3
Per formula unit								
Si	8.78	0.02	7.68	0.01	7.76	0.07	6.85	0.02
Al	3.22	0.02	4.32	0.01	4.24	0.07	5.15	0.02
Ca	0.28	0.02	1.94	0.03	1.79	0.12	3.08	0.03
Na	3.51	0.05	1.86	0.04	1.98	0.11	0.86	0.03
K	0.20	0.01	0.17	0.00	0.18	0.02	0.08	0.02
S	0.01	0.00	0.13	0.01	0.11	0.02	0.14	0.04
Cl	0.83	0.01	0.38	0.01	0.43	0.05	0.00	0.00
C²	0.15	0.01	0.49	0.01	0.45	0.03	0.85	0.04
% Me	11.7	0.5	61.3	0.8	57.8	0.4	84.3	3.1
K/Cl	0.24	0.04	0.44	0.04	0.42	0.15	21.13	0.60
Ca/K	1.40	0.09	11.45	0.02	9.86	0.12	36.92	0.21

¹ Calculated² Calculated

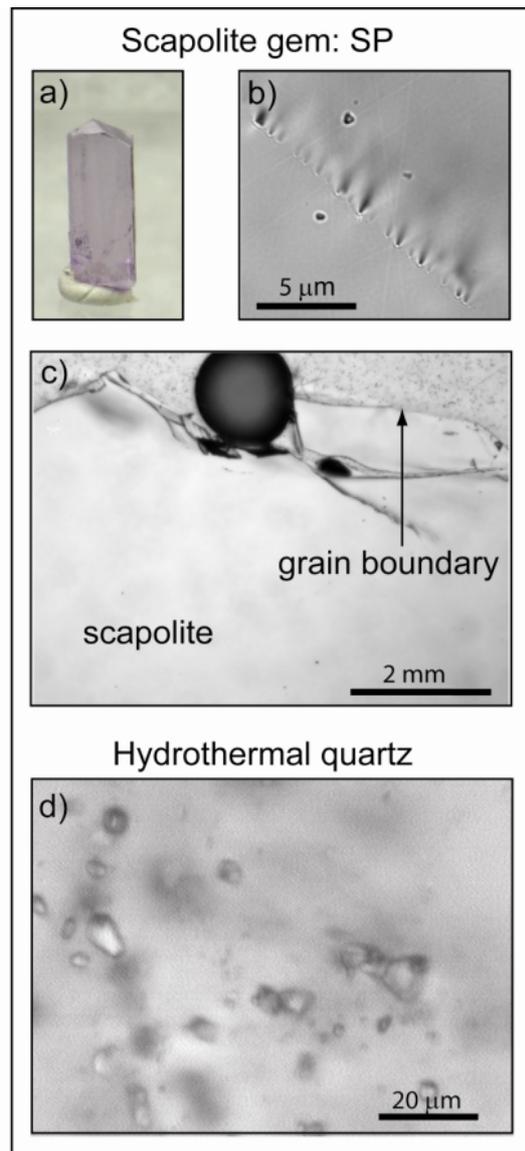


Fig 1. a) Scapolite crystal SP, 0.9 g. b) photo-micrograph showing very minor crystal defect structures in scapolite SP. c) SP contains almost no fluid inclusions. d) In comparison, hydrothermal quartz has abundant fluid inclusions.

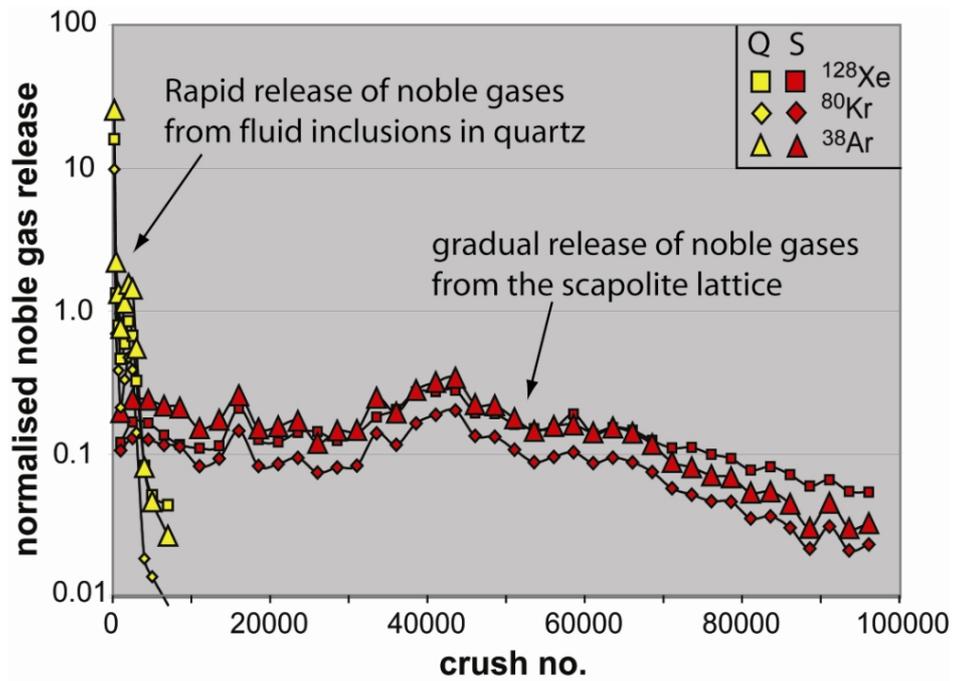


Fig 2. Graph showing the release of halogen-derived noble gases from scapolite (S) and quartz (Q). Note that the rate at which noble gases are extracted from the scapolite lattice decreases during the experiment on the order $\text{Ar} > \text{Kr} > \text{Xe}$. Eg, the extraction profile for ^{128}Xe , which decreases by the least, crosses the extraction profile of ^{38}Ar , which decreases by the most, see text.

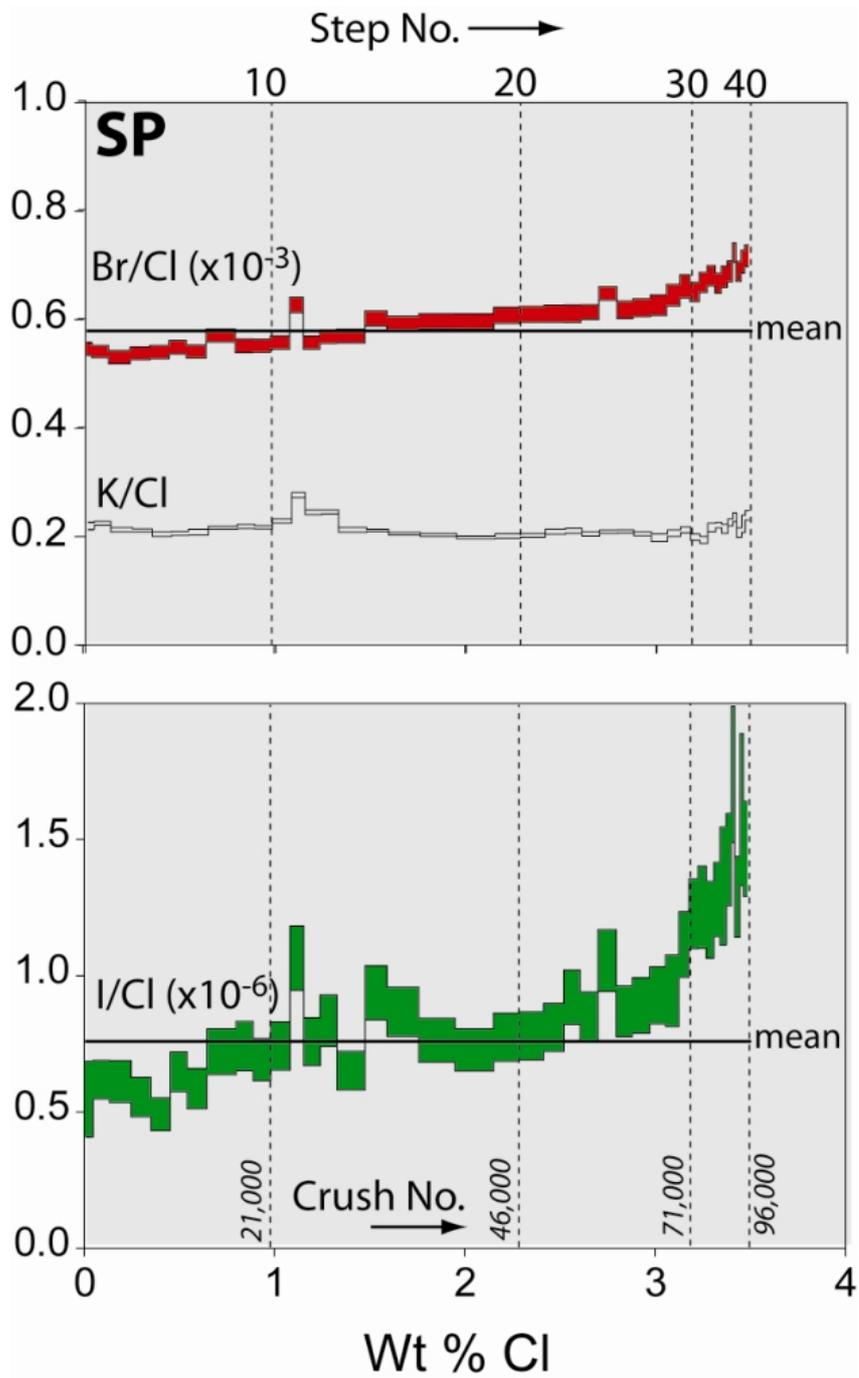


Fig 3. Apparent Br/Cl, K/Cl and I/Cl values versus wt % Cl equivalent. Determined by crushing 7.3 mg of fluid inclusion free scapolite and measuring the potassium and halogen-derived noble gas isotopes: $^{80}\text{Kr}_{\text{Br}}$, $^{38}\text{Ar}_{\text{Cl}}$, $^{39}\text{Ar}_{\text{K}}$ and $^{128}\text{Xe}_{\text{I}}$. Analytical uncertainty is shown (2-3% for Br/Cl and ~10% for I/Cl in this sample), the Br/Cl and I/Cl values obtained from the first 10 extraction steps are reproducible.

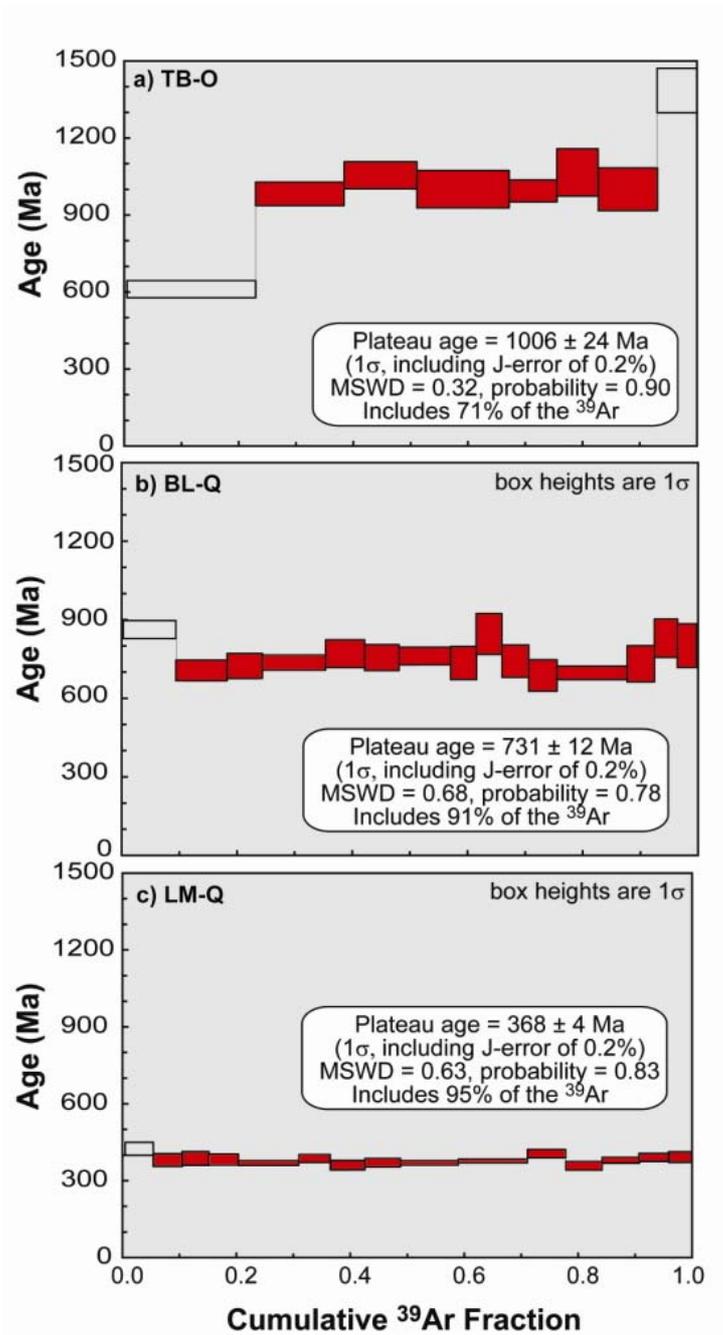


Fig 4. Ar-Ar plateau diagrams for Grenvillian Scapolite.

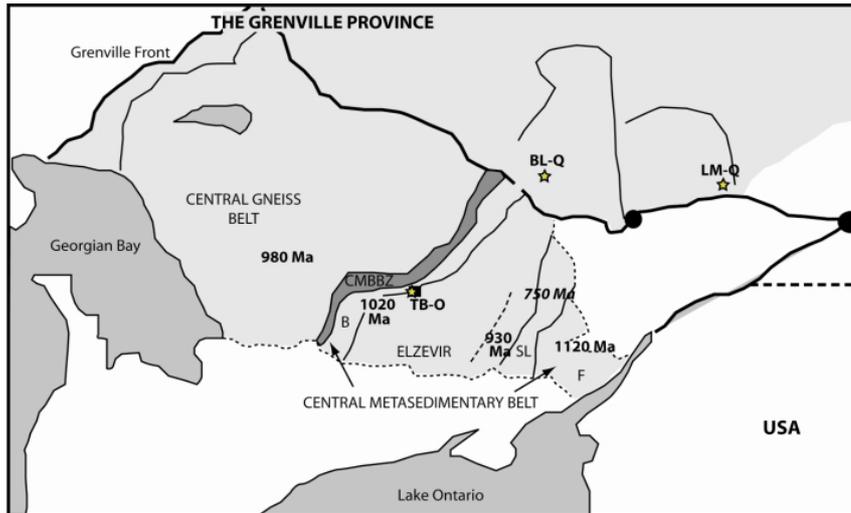


Fig 5. Map of northeast North America showing the 1.2-1.0 Ga Grenville Province and the localities of the scapolite samples TB-O, BL-Q and LM-Q. The Central Metasedimentary Belt is divided into the (B) Bancroft, Elzevir, (SL) Sharbot Lake and (F) Frontenac terranes. The approximate Ar-Ar ages of hornblende are indicated in bold, while feldspar ages are indicated in italic-bold (Cosca et al., 1992; Streepey et al., 2002).