Diverse origins of fluid in magmatic inclusions at Bingham (Utah, USA), Butte (Montana, USA), St. Austell (Cornwall, UK), and Ascension Island (mid-Atlantic, UK), indicated by laser microprobe analysis of Cl, K, Br, I, Ba + Te, U, Ar, Kr, and Xe

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Abstract—Saline fluid inclusions (FI) trapped at close to the temperature of final solidification of a granitic melt occur in rocks from Bingham, Utah, Ascension Island, mid-Atlantic Ocean, and St. Austell, Cornwall. Slightly lower temperature FI occur at Butte, Montana. Argon, Kr, and Xe were extracted from FI by laser microprobe decapsulation of minute portions of the samples after neutron irradiation (along with synthetic FI of known composition), and measured in a low blank, high sensitivity, pulse-counting mass spectrometer. Results enable measurement of Cl, K, Br, and I simultaneously with 39Ar, 38Ar, 40Kr, and 133Xe, in ~10^-7 cc of fluid, the contents of a single spherical inclusion ~57 μm in diameter.

Average K/Cl in Bingham and St. Austell FI are ~0.25 and ~0.15, respectively, broadly consistent with the composition of fluids equilibrated with rocks at temperatures close to the eutectic in the granite system (400-600°C and 0.5-2 Kp). Within-sample variations in K/Cl are significant and may be a result of exsolution of fluids from magmas over a range of temperatures and/or pressures. Halogen ratios are confined to a narrow range, with I/Cl and Br/Cl in Bingham, Ascension, and some Butte FI ~ 1-8 × 10^-2 and 1-3 × 10^-3, respectively, probably evidence of a common source of salinity, presumably part of the Earth's mantle. A component of salinity derived from continental crust may be indicated by higher I/Cl and lower Br/Cl in St. Austell FI. Radiogenic 40Ar produced in situ from K in FI after trapping is usually insignificant. 38Ar, is defined as 36Ar in excess of the amounts attributable to atmospheric gases and that produced by decay of K in FI. Variations in 38Ar/Cl in Bingham, Ascension, and St. Austell FI are greater than can be explained by just different Cl concentrations in FI, typically between ~5 × 10^-7 and 8 × 10^-6), probably because Ar and Cl have been fractionated within these systems by outgassing of a magma in the interval between exsolution of different FI generations. Concentrations of Ar and 40Kr in most Bingham, Ascension, and St. Austell FI are ~2 orders of magnitude greater than in most lavas and granites, with 40Kr/36Ar ranging between ~0.015 and ~0.08, grossly consistent with the composition of fluids exsolved from magmas. Several distinct fluid types are present at Butte: (1) rare 'magmatic' FI having halogen and noble gas abundances similar to Bingham and Ascension and (2) abundant FI having 38Ar and 40Kr concentrations similar to air-saturated fresh waters, with slightly lower Br/Cl than FI at Bingham and Ascension (~5-10 × 10^-4) and relatively high 40Ar/Cl (~1 × 10^-2 and 2.8 × 10^-5). Mixing prior to trapping between fluid derived from magmas and meteoric water that acquired 40Ar, plus some halogenes by interaction with country rocks is the most likely origin of most Butte FI.

INTRODUCTION

Silicate melts contain variable amounts of dissolved water, which reduces the melting temperatures, densities, and viscosities of magmas, thereby facilitating their formation and movement in the Earth. The solubility of water in most magmas declines with decreasing pressure, a situation which can result in exsolution of an aqueous fluid from an ascending melt, particularly when combined with fractional crystallization of volatile-free phenocrysts. Halogens are strongly partitioned into an aqueous phase, and a 'hydrosaline melt' composed of water, halogens, and other volatiles will form under some circumstances. Fluid inclusions (FI) having compositions and filling temperatures appropriate to have been exsolved from igneous melts occur in some granitic bodies, although it is often not clear that these inclusions have formed directly by exsolution from a melt, at what stage of evolution of a magma they may have exsolved, or if contamination of a magma with hydrothermal fluid or wallrocks occurred (summarized in Roeder, 1984, 1992; Bodnar, 1992). The purpose of this report is to document the compositions of high temperature FI from four different granitic bodies, determined using the recently developed laser microprobe noble gas mass spectrometry technique (referred to as LMNGMS), and to explore the constraints that these data provide on the origin of fluids and salts in these FI. Samples studied in this reconnaissance survey include granitic blocks from Ascension Island, mid-Atlantic Ocean, Paleozoic quartz-topaz-tourmaline greisen associated with Cornubian granites of SW England, St. Austell, quartz + sulfide ore-bearing veins from the porphyry copper deposit at Bingham, Utah, and altered quartz monzonite porphyry at Butte, Montana. The samples from Butte, Bingham, and Ascension include some of the earliest reported examples of highly saline, aqueous fluids that may have exsolved from granites (Roedder and Coombs, 1967;
Roedder, 1971). A range of environments containing F1 that originated, at least in part, by exsolution from magmas is represented, including highly saline, high-temperature F1 from Ascension and Bingham, to F1 that may contain fluids derived in part from crustal sources at Butte and St. Austell. Historically, much research on F1 has been conducted on samples from hydrothermal ore deposits and of the four areas studied in this report, only Ascension Island is not a well-known mining district. The association between silicic magmas, saline fluids trapped at high temperature, and some hydrothermal ore deposits has been noted for some time, with a demonstrable, although incompletely understood, genetic relation among the three (for reviews see Whitney, 1989; Candela, 1989; Henley et al., 1992).

In the LMNGMS technique, Ar, Kr, and Xe are extracted from F1 by zapping minerals to deplete the inclusions using a laser microprobe targeted through an optical microscope and measuring the gases released in a high sensitivity mass spectrometer. Concentrations and ratios of noble gas isotopes have previously been used to identify potential sources and pathways of fluids in modern hydrothermal systems (e.g., Zartman et al., 1961; Mazor, 1977; Torgrerson et al., 1989), and although as yet there have been relatively few studies of noble gases in F1 rocks, (Rama et al., 1965; Harper and Schamel, 1971; Stuart and Turner, 1992), it is clear that rare gas isotope geochemistry of fluids trapped in minerals has promise for improving our understanding of ancient hydrothermal systems. The noble gases found in a magmatic sample could potentially come from many sources, ranging from primitive (original) mantle to the modern atmosphere. Radioactive decay and in some special circumstances, nuclear reactions (e.g., transmutation of 37Cl to 36Ar by neutron capture), can also produce some of these isotopes. Partitioning of noble gases between coexisting phases in a silicate melt/saline melt/vapor system at 500°C or greater are certain to be different than in an air/water system at surface temperatures, but this is a little-studied field with few relevant measurements.

In a procedure similar to that used in 40Ar/39Ar age determination, the abundances of a group of elements (Ca, Cl, K, Br, Se, I, Ba, Te, U) and some naturally occurring noble gases (36Ar, 38Ar, 40Kr, 129Xe) can be measured simultaneously in pile-irradiated rock samples (Turner, 1965). The utility of simultaneous analysis of natural variations in isotopic abundances of Ar and other elements in neutron-irradiated F1 was demonstrated by Kelley et al. (1986), who correlated distinct dissolved 40Ar components in F1 with Ca, Cl, and K. Subsequently it was shown that measurement of the abundances of halogens in F1, Br, and I) in F1 is particularly useful, as they are relatively conservative tracers of fluids in hydrothermal systems (Böhlke et al., 1989; Böhlke and Irwin, 1992a). Although there exists a large database for halogens in fluids (e.g., White et al., 1963), and in aqueous solutions at low temperatures, halogen chemistry is relatively straightforward (see Fuge, 1974; Fuge and Johnson, 1986 for review), there are relatively few studies of halogens in rocks, particularly Br and I. The effects of phase separation at high temperatures, be it solid/liquid or liquid/vapor remain poorly known (e.g., Honda, 1970). Some magmatic minerals take up significant quantities of Cl (hornblende, biotite, apatite), but effectively reject Br and I; alteration of an igneous rock may impound or release halogens, removal of water from a fluid phase during rock alteration may increase halogen concentrations in the remaining fluid and fractionate elements; magma degassing may preferentially remove Cl (as HCl) from the well-known interaction of NaCl solutions and silica (see Burnham, 1979, for review), and finally, highly concentrated magmatic brines may precipitate NaCl that does not contain significant amounts Br or I (the "halite effect" of Cloke and Kesler, 1979). Metamorphic or sedimentary processes may also have affected halogen abundances in any natural fluid. Some sediments may contribute significant I to formation waters and since I can be present in very low concentrations, even an atmospheric source of I is possible (from methyl iodide, Heumann et al., 1990).

The samples studied have several distinct types of F1 intermixed. High salinity F1 containing halite ± other daughter minerals (hereafter referred to as "salt-rich") occur intimately associated with F1 dominated by vapor plus variable amounts of liquid ("vapor-rich"). Although these two F1 types are generally interspersed in these samples on too small a scale to permit analyzing a pure sample of a given type using the current LMNGMS technique, we believe that some, and possibly many, of the analyses are of small groups of F1 that are dominantly of one type. In any case, the importance of microanalysis is demonstrated by the large variations in isotopic and elemental abundances that occur over distances of less than a millimeter within samples. A preliminary account of the abundances of halogens, Ar, and Kr was presented by Irwin and Böhlke (1992).

METHODS

The LMNGMS technique has been previously described in detail (Kirschbaum, 1988; Irwin and Böhlke, 1991; Böhlke and Irwin, 1992b; Irwin and Reynolds, 1995), and only methods specific to the samples analyzed will be outlined here. Samples typically ~1 cm in diameter and several mm thick were cut from the "butt ends" reaming from slide mounts, minimally polished, photomicrographed, and neutron-irradiated, along with the irradiation monitor standard hornblende Hb3Gt and synthetic F1 containing known concentrations of Cl, Br, I, and K. The possibility of contamination by organic compounds precludes the use of standard doubly polished plates and petrographic control of the specific F1 types in samples selected for analysis was minimal. All of the data from each Bingham, Butte, and Ascension Island samples are from single rock chips designated by sample numbers on figures and in the text, whereas the St. Austell data are from several different chips from a single hand specimen. Samples are described in more detail in the Appendix. Noble gases were extracted from neutron-irradiation monitors, microstandards, and natural and synthetic F1 using a Q-switched Nd:YAG laser microprobe targeted through an optical microscope. The laser was fired 3-30 times at a given point or a small area within a sample, creating an area of fracturing and cratering in the host mineral of between ~10^-2 and ~10^-3 cc in volume, the contents of a cylinder of the host mineral ~100-300 μm in diameter and ~50-150 μm deep. The form of laser craters is similar to that shown in photomicrographs in Irwin and Böhlke (1991) and Böhlke and Irwin (1992b), although due to a combination of the higher neutron fluence in irradiation and the high population density of saline F1 in these samples, the volume of host mineral from which gases were extracted is less than in these prior studies by a factor of more than 5. In some analyses, it was possible to view and target small groups of F1 (3-5), using the microscope associated with the laser microprobe. It is generally possible to avoid fractures and areas of inclusions of other minerals. Data from synthetic F1 and previous studies demonstrate that signif-
Values are listed only for parameters likely to yield meaningful comparison with Fl, and for which published analyses are available or can be estimated from previous studies.

\[ ^{40} \text{Ar}_{40} \text{Ar} \text{Cl} \] is the lowest and highest values for a given ratio measured in the sample listed

\[ ^{40} \text{Ar}_{40} \text{Ar} \text{Cl} \] is from the slope of mixing lines on three isotopic correlation plots.

\[ ^{40} \text{Ar}_{40} \text{Ar} \text{Cl} \] and \( ^{129} \text{Xe}_{40} \text{Ar} \) shown in this table are the measurements furthest from the composition of "air" on these plots, analyses that appear to be least affected by atmospheric contamination.

The mean and range of K/Cl excludes analyses where sampling of K-bearing solid inclusions is known or suspected from K abundances.


* I/C in Fl amphibole in Ascension I. sample ER63-133-4 is 6.83 and 6.59 x 10^-3.

Table 1.

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Details of the pile irradiation procedure and data from solids presented in a separate publication (Irwin and Reynolds, 1985). The precision of measurement of K/Cl in synthetic F1 is ±1.5%. The standard deviation of I/Cl in synthetic F1 is ±9.2%. but there is an additional uncertainty in measuring 129Xe caused by low concentrations of I typical of these migmatic F1, which means that the uncertainty in measurement of I/Cl is ±10 - 15%. Analyses yielding count rates for 129Xe that are more than a factor of 3 lower than standards are not included in figures or tables because of their larger uncertainty. This selection procedure rejects some analyses with low I/Cl in the most I-poor samples (Bingham 207a, 208, Ascension, Butte), which may introduce a minor bias in the dataset. This bias, if present at all, is relevant to only a small subset of the data with I/Cl < 1 - 3 x 10^-3.

Previous studies in this and other laboratories have shown that atmospheric gas is trapped in most F-bearing samples. This gas is not always completely removed during bakeout of the sample system and it is thought that air is trapped along annealed fractures and is released by laser sampling. Cumulative experience has proven that repeated bakeouts conducted over an extended period of time tend to progressively reduce the amount of air-like gas released from samples, until, if at least some cases, there is very little or no evidence of atmospheric contamination (e.g., Böhlke and Irwin, 1992c). Much of the data gathered in this study are from samples that were baked three or more times (each of which was for 3 - 5 days at greater than 100°C), with many of the least "air-like" analyses measured in the final stage of sampling. Qualitatively, samples having a lower degree of polish are less likely to contain atmospheric gases, but this is not always true, as some unpolished cleavage flakes of fluorite contain significant amounts of air contaminant (Böhlke and Irwin, 1992c).

Air contamination has virtually no effect on measurement of abundances of Cl, K, Br, Ba + Te, U, and I, as the abundances of pile-produced 40Ar, 80Ar, 88Kr, and 129Xe are one to three orders of magnitude greater than gases originally in the samples, but complicates measurement of some ratios in Fl, such as 40Ar/80Ar and 88Kr/88Ar.

Complete data tables for noble gases and other elemental abundances are rather bulky and have been stored in archival form with the journal. Table 1 is a summary of data from each sample and some other terrestrial volatile reservoirs.

BINGHAM, UTAH

Background

At Bingham Canyon, a large body of porphyry Cu and Mo sulfide ores is associated with a composite, hydrothermally
component, described as “formation water” (Bowman et al., 1987).

Three samples were studied; two were collected less than 10 meters apart from vuggy quartz veins from near what was then the bottom of the open pit in 1963 (ER63-207a and ER63-208), and one from a veinlet in the main body of the pit (ER62-14). These samples are similar to but not true splits of samples described in Roedder (1971). The presence of dense, salt-rich, aeous FI trapped at close to the eutectic temperature in the granite system, such as some of these FI from Bingham, is evidence that fluids may be exsolved directly from magmas in the final stage of crystallization of granite (reviewed in Roedder, 1992). Coexistence of salt-rich and vapor-rich FI intimately intermixed in magmatic-hydrothermal systems has been interpreted as evidence that an earlier fluid separated into low and high density fluids at close to the time of FI trapping, presumably due to a slight decrease in pressure or temperature (reviewed in Roedder, 1984). It has also been suggested that the close spatial association of different FI types in porphyry systems is due to different stages of fluid trapping (Roedder, 1971; Ahmad and Rose, 1980).

Aside from the fact that there are no previous studies of halogens or noble gases in FI from this type of magmatic-hydrothermal system, specific questions about FI at Bingham include the contributions of magmatic, meteoric, and formation waters, the significance of the multiple generations of FI that characterize these samples, and the possibility of testing the hypothesis that FI dominated by vapor and by liquid + salt in the same samples originated from boiling or condensation of a common parent fluid.

### Halogens

In general, Br and Cl are strongly correlated, with some relatively subtle variations in Br/Cl within samples, and

![Fig. 1. Abundances of Br and Cl (in atoms) in Bingham FI. In all of these plots, the absolute abundance of an element is expressed in exponential notation, i.e., 1.24E+012 is 1.24 × 10^{12} atoms. Linear data arrays through the origin indicate constant element ratios. The data illustrate similar Br/Cl in most FI from samples 208 and 207a over a large range of Cl abundances, whereas FI in 62-14 have higher Br/Cl. Composition of seawater, (Br/Cl = 0.00154), Br/Cl = 0.001 and Br/Cl = 0.003 shown for reference.

In plots involving halogens and K, uncertainties are largely a function of uncertainty in the pile-irradiation production rates (a constant), plus uncertainties in extrapolation of count rates to the time of admission of gases into the mass spectrometer, which are also relatively constant over the range of abundances of halides and K within each study area, hence the errors are nearly a constant proportion of the amount of Cl, Br, I, K shown, and enlarged parts of figures do not usually have much larger error bars.

![Fig. 2. l/Cl vs. Br/Cl in Bingham FI. Symbols as in Fig. 1. The trend of covariation of l/Cl and Br/Cl that would be caused by selective removal (or dissolution) of Cl-bearing phase(s) is shown, (the “halite effect” of Cloke and Kesler, 1979). If l is excluded from crystallizing solids to a greater degree than Br (due to its larger ionic radius) in an evolving fluid or magma, l/Cl will increase more than Br/Cl, which might account for the general trend of observed variations in these ratios (see text).](image-url)
larger variations between samples (Figs. 1, 2). Similar Br/Cl and I/Cl are indicated Fl in samples 207a and 208, with the mean values for these ratios overlapping at the one standard deviation level (Fig. 2; Table 1). Fluid inclusions in sample 62-14 have Br/Cl and I/Cl distinctly greater than 207a and 208 (Figs. 1, 2). Fractional crystallization of Cl-bearing phases (i.e., hornblende, biotite, apatite) or of halite itself, prior to inclusion trapping, will cause correlated increase in Br/Cl and I/Cl (the "halite effect" of Cloke and Kesler, 1979). The scarce experimental data indicate that I is excluded from halite to a greater degree than Br by approximately an order of magnitude (i.e., I/Cl in halite is lower than Br/Cl in halite by a factor of 5–10, Holser, 1979), and thus, it is possible that most of the measured variations in I/Cl and Br/Cl between and within samples are caused by crystallization of (or dissolving) Cl-bearing phases in the magma and/or hydrothermal solutions. The same effect may also be true for partitioning of Cl, Br, and I between a magma and an aqueous fluid phase, as HCl is strongly partitioned into the aqueous phase (see Burnham, 1979, for review), and this may not be equally true of HBr and HI. Alternatively, an additional or different source of salinity for Fl in sample 62-14 is possible. Many fine-grained sedimentary rocks and fluids derived from them have I/Cl much greater than Fl in samples 207a and 208, as does the average continental crust, and incorporation of formation water derived from the sedimentary country rock (Bowman et al., 1987), or pendants of wallrock into a magma could cause the increased I/Cl.

There appears to be significant variation in Br/Cl, with no change in I/Cl in sample 208, but due to the low abundance of I in this type of Fl, I/Cl ratios may not be measured accurately enough to confidently state that this is the case. If real, these uncorrelated variations are probably of Fl derived from different magmas.

Potassium and Chlorine

In most analyses, K/Cl is close to 0.25 (Fig. 3), with a few showing higher K/Cl, interpreted as the result of sampling of heterogeneously distributed, relatively rare, K-bearing solids such as mica. Abundances of Cl, Br, I, K, and ratios of these elements to $^{39}$Ar and $^{40}$Kr are inconsistent with incomplete Fl outgassing or heterogeneous sampling of Cl-bearing solids (i.e., halite, sylvaite), by the laser causing these subtle variations in K/Cl. The mean and standard deviation of K/Cl in sample 207a and 208 are similar (0.251 ± 0.02 for 207a, 0.231 ± 0.025 for 208). Excluding obviously high values, average K/Cl = 0.276 ± 0.061 in Fl in sample 62-14, within the range of the other samples. These ratios are slightly higher than any measured by Lagache and Weisbrod (1977), but in experiments with Na-KCl solutions buffered by synthetic quartz monzonite, sulfides and magnetite, Henley et al. (1992), obtained K/Cl between 0.19 and 0.32 at 500–600°C and 1–2 Kb. Variations in K/Cl are not correlated with any other parameter measured and could be related to changes in pressures and/or temperatures in the source of the fluid, or substitution of elements such as Ca or Fe in some Fl. Proportions of liquid, vapor, and salts are variable in Bingham Fl, consistent with trapping of Fl over a range of pressures and temperatures (reviewed by Bodnar, 1994).

**Argon, Krypton, and Chlorine**

In previous studies of Fl, correlations between argon isotope ratios and Cl, K, and Ca have been used to define and distinguish between Fl types (Kelley et al., 1986; Böhlke and Irwin, 1992c; Turner and Bannon, 1992). Fluid inclusions at Bingham are complex, with multiple generations of annealed fractures containing Fl that have variable proportions of vapor, liquid, and daughter minerals present within each rock chip. These complexities give reason not to expect simple patterns or correlations in the ratios of gases and of gases to Cl. Nonetheless, many of the data from each of the samples studied fall close to two-component mixing lines between air and components having distinct $^{39}$Ar/$^{40}$Ar ratios (Fig. 4). $^{39}$Ar, is defined as $^{39}$Ar in excess of the amounts attributable to atmospheric gases (295.5 times $^{40}$Ar) and that produced by decay of K in the sample since the Fl were trapped ($^{40}$Ar). In this and previous studies of noble gases in Fl, there is a component of gas of atmospheric composition that affects many of the analyses (Turner and Bannon, 1992; Böhlke and Irwin, 1992b,c). Previous experience has demonstrated that air-contaminated analyses could be identified and that the composition of Fl free of air-contamination could be determined by use of three-isotope correlation plots such as Fig. 4 (see Böhlke and Irwin, 1992b,c), but in this study, some analyses of $^{39}$Ar/$^{40}$Ar are similar to atmospheric, with $^{40}$K/$^{39}$Ar very different from air and vice versa. Throughout this paper, emphasis is placed on $^{40}$Ar/$^{39}$Ar ratios defined by the slope of mixing lines which are not compromised by air contamination and other ratios that are furthest from "air" on three-isotope correlation plots, which are probably (but not necessarily) free of air contaminant, and in the least provide a basis for comparison of data within and between samples. Information may be omitted from consideration by this pro-
between ~1 and ~3 \times 10^{-7} \, \text{cc/g} of $^{36}\text{Ar}$. We are not aware of any direct experimental determination of partitioning of noble gases (or halogens) between magmas and fluids exsolved from them, but vesicles in basaltic glasses typically contain concentrations of Ar and Kr ~2 orders of magnitude greater than the lavas in which they are trapped (Staudacher and Allègre, 1989; Staudacher et al., 1989). Concentrations of $^{36}\text{Ar}$ listed above are between 1 and 3 orders of magnitude greater than most basic lavas (see Kyser and Rison, 1982; compilation of Kaneoka and Takaoka, 1991), and the few granites studied to date (Kuroda et al., 1977), and approximately an order of magnitude lower than air-saturated fresh waters (c.f. Turner and Bannon, 1992; Burgess and Parsons, 1994; section on Butte in this report), consistent with an origin of these fluid by exsolution from magmas.

Within samples 207a and 62-14 the magnitude of variations in $^{40}\text{Ar}/\text{Cl}$ is within the range expected from differences in salinity of FI (approximately a factor of ~5 for both, Fig. 4), evidence that in some extractions the laser has sampled fairly homogeneous groups of just salt-rich and just vapor-rich FI that contain a uniform concentration of $^{40}\text{Ar}$. In contrast, $^{40}\text{Ar}/\text{Cl}$ varies by a factor of more than 15 within sample 208 and between samples 208 and 207a, a greater degree of variation than can be explained by just different Cl concentrations in FI, probably because $^{40}\text{Ar}$ and Cl have been fractionated within this system in the interval between production and trapping of different generations of fluid.

In most previous studies of noble gases in fluids and FI, $^{84}\text{Kr}/^{36}\text{Ar}$ usually ranges between the atmospheric value (~0.02) and that of air-saturated waters (~0.04) (Smith and Kennedy, 1985; Hiyagon and Kennedy, 1992; Böhlke and Irwin, 1992; Stuart and Turner, 1992; Burgess and Parsons, 1994). Although many Bingham FI are also in this range, $^{84}\text{Kr}/^{36}\text{Ar}$ varies between less than atmospheric and twice that of air-saturated waters (Figs. 5, 6; Table 2), similar to the composition of lavas (Kyser and Rison, 1982; Allègre et al., 1986; Staudacher and Allègre, 1989), gases derived from magmas (Matsubayashi et al., 1978; Kaneoka, 1980), and FI in mantle nodules (Kaneoka and Takaoka, 1978). Unlike previous studies, $^{84}\text{Kr}$ is not well correlated with $^{40}\text{Ar}$ or Cl in these magmatic FI. If vapor-rich and salt-rich FI in these samples formed by phase separation of a common, parental brine, by analogy with partitioning of Ar and Kr between air and aqueous brines, correlated variations in $^{84}\text{Kr}$, Cl, and Ar might be expected, with low-density FI having lower $^{84}\text{Kr}/^{36}\text{Ar}$ than higher density FI, although we are not aware of any experiments that constrain this effect at magmatic temperatures, which may be minimal or in the opposite direction. In Bingham FI, $^{84}\text{Kr}$ is not correlated with Cl or Ar (Fig. 6). A fluid phase exsolved from a magma has higher $^{84}\text{Kr}/^{36}\text{Ar}$ than the magma, as the lighter rare gases are more soluble in silicic melts than heavier gases (Lux, 1987), hence, some of the higher $^{84}\text{Kr}/^{36}\text{Ar}$ values could be fluids exsolved from a melt, but $^{84}\text{Kr}/^{36}\text{Ar}$ is often lower in FI than in most silicic melts. A large, cooling pluton may "degas" in several or multiple stages and fluids exsolved from a magma that had previously exsolved a fluid phase would be expected to have relatively high Cl/$^{36}\text{Ar}$ and low $^{84}\text{Kr}/^{36}\text{Ar}$. The wide range in Kr, Ar, and Cl ratios probably indicates that no single process such
Chemical evidence for the origin of fluid inclusions

(a) 2.5E+006

(b) 4.0E+005

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Fig. 5: Abundances of 36Ar and 36Kr in Bingham FI (atoms). Symbols as in previous figures. Linear data arrays through the origin indicate constant element ratios. Also shown for reference are the ratios of the atmosphere (air: −0.02) and of 10°C air-saturated fresh water (ASW: −0.04). Most of the data are between these values, but some FI have 36Kr/36Ar greater than air-saturated water and some are less than atmospheric.

as phase separation or outgassing of a magma can account for the measured variations within each sample.

40Ar/39Ar Age of Hydrothermal Alteration

Bingham FI are dominated by 40Ar, and/or atmospheric gases, with 40Ar typically 10% or less of the total 40Ar, which effectively precludes calculation of meaningful ages from gases extracted from FI. In samples 62-14 and 208, quartz occurs in a fine-grained matrix of alteration minerals which contain several weight percent K (which could be either the potassic alteration assemblage or sericitic alteration; see Moore and Nash, 1974; Bowman et al., 1987). Gases were extracted from this matrix using the same procedure and crater size as in FI. Kelley et al. (1986) demonstrate that by correcting 40Ar for 40Ar, using the 40Ar/36Ar ratio in FI, meaningful 40Ar/36Ar ages can sometimes be calculated. Some limitations of this approach in complex samples are illustrated by analyses of matrix material which yield valid ages only when 40Ar, is a small fraction of the 40Ar measured. Dates calculated from extractions in which the correction for 40Ar is <10% of the total 40Ar are 37.7 ± 1.4 Ma, 37.4 ± 2.8 Ma for sample 208, and 39.9 ± 2.9 Ma for sample 62-14, the same as K-Ar ages of biotite from monzonitic intrusions and latite dikes in the pit at Bingham, which average 37.4 ± 0.6 Ma and 38.3 ± 1 Ma, respectively (data from Moore et al., 1968, recalculated using the decay constants of Steiger and Jager, 1977). In contrast, in extractions where 40Ar is a significant fraction of the total 40Ar (>20%), “apparent ages” are 63.5 ± 4.0 Ma and 134.2 ± 5.4 Ma if 40Ar is adjusted for 40Ar, using the mean 40Ar/36Ar of each sample.

Evidence of an Evolving Magmatic-Hydrothermal System at Bingham?

Each of the three Bingham samples studied is characterized by a different average FI composition, with distinctions between samples that can be explained by processes known to occur in this type of hydrothermal system. Average halogen and K/Cl ratios in FI in samples 207a and 208 overlap, suggesting a common source, but in sample 208, average 40Ar/36Ar is approximately a factor of 15 less than sample 207a, with 40K/36Ar slightly lower as well, (average of 0.027 and 0.036, respectively). These distinctions are both qualitatively consistent with outgassing of a common “parent magma” in the interval between exsolution of the FI in samples 207a and 208. In a similar manner, FI in sample 62-14 typically have higher Br/Cl, I/Cl, and 40Ar/36Ar than sample 208 by factors of...

Fig. 6: Isotope correlation plot of 36Ar/40Kr vs. Cl/36Ar in Bingham FI. Symbols as in Figs. 1–3. The arrows showing potential effects of phase separation and magma outgassing are intended to be purely symbolic and represent the general direction of change in a system caused by these processes. "Outgassing" refers to a hypothetical situation: if a magma "outgasses" by exsolving a low density phase similar in composition to the vapor-rich FI found in many magmatic hydrothermal systems, this exsolved phase will have relatively high 36Ar/40Kr compared to the magma and will leave behind a magma with higher Cl/36Ar. Hydrosaline melt phases subsequently exsolved from this magma should have lower 36Ar/40Kr and higher Cl/36Ar. Similarly, "phase separation" refers to the effects of separation of a hydrosaline melt into lower and higher density phases: there will be large variations in Cl/36Ar between a low salinity, vapor-rich fluid and a salt-rich fluid, with possibly some fractionation between K and Ar. Presumably Kr will be partitioned into the higher density phase, but the direction and magnitude of this effect in a hydrosaline melt at magmatic temperatures remain unknown.
of between ~2.5–5, differences that could be explained by crystallization of a solid phase containing Cl in a magma or brine in the interval between generation of the fluids in these two samples. If this mechanism is relevant, more than half of the Cl initially present in a fluid or magma must have been incorporated into solids, which might be accomplished by either crystallization of a relatively small amount of halite from a brine, or a large quantity of Cl-bearing phenocrysts (i.e., biotite, hornblende, apatite), from a magma.

**Background**

The porphyry system at Butte, Montana consists of a large, composite igneous complex (the Boulder batholith), parts of which have been intruded by multiple generations of later veins and dikes with associated alteration halos. For reviews of the regional geology and detailed studies of mineralization at Butte see Meyer et al. (1968) and papers in Miller (1973). Intrusion of the Boulder batholith took place between 78 and 68 Ma (Tilling et al., 1968), with hydrothermal activity and associated mineralization occurring 5–10 Ma after the late plutons and continuing for millions of years later, as evidenced by argillic alteration of dikes dated at 40–48 Ma (Meyer et al., 1968). There is a relatively minor component of 206Pb, 207Pb, and 87Sr in this batholith, which could be derived from either older crust or the mantle (Doe et al., 1968; Zartman, 1974). Fresh plutonic rocks in the Boulder batholith have δ18O and Δδ values consistent with a magmatic origin (Garlick and Epstein, 1968; Sheppard and Taylor, 1974). In contrast, hydrogen and oxygen isotopes in quartz and hydrothermal minerals in the area of the Butte ore deposits illustrate the pervasive influence of meteoric waters, with little evidence of a magmatic origin remaining (Sheppard and Taylor, 1974). Overprinting of magmatic isotopic signatures by meteoric water associated with hydrothermal mineralization at Butte contrasts with Bingham, which yields some oxygen and hydrogen isotope ratios consistent with magmatic temperatures. Fluid inclusions at Butte generally have lower homogenization temperatures than the other granites studied (most are less than 500°C and some less than 300°C), with no evidence of “boiling” observed (Roberts, 1975). Most of the Butte FI studied are dominated by liquid + vapor FI, with two distinct populations containing different proportions of these phases present in both samples (see Appendix). The melting temperatures of ice in FI suggest an average salinity of ~8.5 wt% NaCl, which we take to be an upper limit, due to the presence of CO2 (see Appendix).

**Halogens and Potassium**

Chlorine, Br, and I concentrations in quartz are approximately an order of magnitude lower than the samples from Bingham, consistent with the lower population density and salinity of FI. Average Br/Cl and I/Cl are similar to FI from Bingham and Ascension Island (see other sections of this paper; Table 1), with slightly lower Br/Cl and higher I/Cl. Variations in I/Cl and Br/Cl within samples are not well correlated. The distinction in halogen abundances between the two samples is poorly defined but sample 322 has lower mean Br/Cl (0.944 ± 0.2 × 10−3 vs. 1.149 ± 0.23 × 10−3, Fig. 7), and higher I/Cl than 323 (4.24 ± 0.72 × 10−5 vs. 3.73 ± 0.65 × 10−5), consistent with the different FI populations in this sample (see Appendix for sample descriptions), and a larger contribution of halogens from a “crustal” source, as elaborated in the next section.

Most analyses of Butte yield K/Cl greater than any likely natural values for fluids of this temperature and salinity, which is probably due to extraction of 40Ar from mica inclusions in quartz in these samples. The lowest K/Cl measured in Butte FI (~0.23) is similar to fluids in equilibrium with quartz monzonite, sulfides, and magnetite at 400–600°C and 1–2 Kb (Hemley et al., 1992).

**Argon, Krypton, and Chlorine**

As discussed in earlier sections of this report, it is not clear that atmospheric contamination has been eliminated, but in view of past experience (see Methods section), we believe that some endpoints of mixing lines furthest from “air” on isotope correlation diagrams are close to air-free analyses of FI. Most Butte FI define a restricted compositional range, with two distinct linear trends and some intermediate values evident in isotope correlation plots (Fig. 8). These compositional variations are interpreted to be a consequence of sampling of different FI assemblages. With one exception discussed later, the FI furthest from “air” have Cl/40Ar ~ 1.5 × 107 (endpoints labelled “A” and “B” on Fig. 8). Combining FI salinity determined by freezing point depression (see Appendix) and FI abundances measured by LMNGMS gives the quantity of fluid analyzed, from which noble gas concentrations are calculated. If we assume an average salinity of 8.5 wt% NaCl equivalent (an upper limit on FI salinity, see Appendix), FI assemblages “A” and “B” must both contain 2.17 × 1014 cc 40Ar per Kg of fluid. Considering the variations in salinity and the uncertainty associated with these measurements, these concentrations of 40Ar are remarkably close.

![Fig. 7. Abundances of Br and Cl (in atoms) in Butte FI. Linear data arrays through the origin indicate constant element ratios. In some FI, Br/Cl is similar to seawater, (Br/Cl = 0.00154), some FI from Ascension I., Bingham and estimated average “mantle” composition; others are as low as ~2/3 of this value, interpreted as evidence of some Br-poor salts derived from the crust.](image-url)
chemical evidence for the origin of fluid inclusions

to air-saturated fresh water at 5-10°C (Fig. 8; for Ar solubilities see Weiss, 1970; Smith and Kennedy, 1983), clear evidence of an origin of these Fl as low salinity waters derived from near the surface.

One of the analyses of Butte Fl in sample 322 yields 40Ar/36Ar = 1.027 and Cl/36Ar = 6.1 x 10^5. This is similar to the composition of some truly "magmatic" Fl at Bingham and Ascension, a Fl type that is observed in this sample very rarely. Brinmhall and Ghiorso (1983) demonstrate that both magmatic gases and meteoric water are involved in the "Main Stage" alteration event at Butte, which has also been suggested for other metal porphyrins (Henley and McNabb, 1978; Dilles and Einaudi, 1992, and references therein).

Most of the Butte Fl contain more 40Ar than can be accounted for just by mixing between saline "magmatic" fluid and meteoric water (Figs. 8, 9). Some potential sources of 40Ar include carbonic fluids associated with some magmas (40Ar/Cl greater than 10^5) in mantle nodules and diamonds, Turner et al., 1990), fluids similar to those associated with natural gas traps in the foreland of the Canadian Rockies (Hiyang and Kennedy, 1992), and low salinity Fl typical of many metamorphic rocks (Irwin, 1994). The Butte samples do not contain inclusions that resemble these fluid types (undiluted), or other low salinity inclusions that might have high

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**Fig. 8.** 40Ar/36Ar vs. Cl/36Ar in Butte Fl, symbols as in Fig. 7. Linear arrays through the composition of "air" represent mixtures of air contaminant and gases extracted from Fl. 40Ar/Cl of Fl is equal to the slope of the mixing line. Radiogenic 40Ar derived from the decay of K has been subtracted from all of the data using 40ArK = 3.9 x 10^9 (457 Ma) although it is usually negligible.

The points labelled A and B are interpreted to be minimally contaminated by air and close to the composition of different Fl assemblages present in different proportions in samples 322 and 323 (see text and Appendix). The line labelled "0-20°C fresh ASW" is the ratio of Cl to 40Ar in fluids that began as air saturated fresh waters over this temperature range and which subsequently acquired 6.0 wt% NaCl. The single data point at 40Ar/36Ar = 1030 and Cl/36Ar = 6 x 10^5 is similar to the composition of some "magmatic" Fl from Bingham and Ascension (other sections of this report), which are rarely observed in sample 322.

Also shown are the approximate compositions of some other fluids: "saline magmatic fluids" is from other sections of this report, "Tertiary brines" is the mean composition of Fl from salinity-bearing veins at Creede, Colorado, Fl from deep drill cores at the Salton Sea, California, and Fl from Hackenburg, New Mexico (J. Irwin, unpubl. data, Fl are described in Böhlke and Irwin, 1992a, 1992c). "Carbon magmatic fluids" and "metamorphic fluids" is the approximate composition of Fl in mantle nodules and low salinity fluids typical of Fl in Paleozoic and Precambrian metamorphic rocks (references cited in text).

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**Fig. 9.** 40Ar/Cl vs. Br/Cl in Butte Fl, symbols as in Figs. 7, 1, and 13. 40Ar is "excess 40Ar", the measured abundance of 40Ar that produced from in situ decay of K and any possible contribution from the atmosphere.

The range in Br/Cl and 40Ar/Cl in these samples is interpreted as evidence of heterogeneous sampling by the laser of three distinct populations of Fl; two different Fl assemblages that began as air-saturated water and acquired salinity plus 40Ar in the subsurface, and an assemblage of saline, magmatic Fl that typically have 40Ar/Cl ~ 5 x 10^5 and Br/Cl ~ 0.0016 (see text for discussion and Appendix for Fl descriptions). These three Fl types are interpersed in variable proportions in these samples. A and B correspond with endpoints of mixing lines on Fig. 8. "Formation waters" is the composition of a hypothetical brine containing relatively high concentrations of 40Ar, and low Br/Cl acquired from protracted interactions between fluid and rock in the subsurface (see text).

Also shown for comparison is the composition of "Tertiary evaporitic brines", the average of Fl from the Salton Sea and Hansenburg, New Mexico.

Measurements having significantly larger uncertainties (resulting from combined errors in 40Ar, 40Ar, Cl and Br) are omitted from this figure.
$^{40}\text{Ar}/^{36}\text{Cl}$, hence, the different types of fluid necessary to explain the abundances of noble gases in Butte FI must have mixed prior to trapping.

Because of the complex history of intrusion and hydrothermal activity at Butte, it is difficult to correlate variations in $^{40}\text{Ar}/^{36}\text{Cl}$ with specific events on rock types. Sample 322 is highly altered and retains relatively little of its igneous character and is dominated by vapor-rich FI that are most distinct from the "magmatic" type in both $^{40}\text{Ar}/^{36}\text{Cl}$ and Br/Cl, (Fig. 9), but also contains very rare FI that are "magmatic" in character (see Appendix, Fig. 8). The lowest values of Br/Cl are from FI that have highest $^{40}\text{Ar}/^{36}\text{Cl}$ (Fig. 9). Bromide-depleted brines are commonly produced by dissolution of halite-bearing evaporites, (see White et al., 1963), and some metamorphosed pelites also have Br/Cl less than seawater (e.g., Boness et al., 1991). Turner and Bannister (1992), outline the principles of using $^{40}\text{Ar}$, concentrations as an indicator of fluid provenance and suggest that ratios between $^{40}\text{Ar}$, K, and Cl can be used to define fluid sources and histories. For K/Cl of the "average" continental crust (150, Parker, 1967), $^{40}\text{Ar}/^{36}\text{Cl}$ of 1.0 $\times$ 10$^{-6}$ and 2.5 $\times$ 10$^{-6}$ (points "A" and "B" on Figs. 8, 9), correspond with fluid "residence times" of 10 Ma and 25 Ma, respectively. For K/Cl more typical of carbonate host rocks (18, Parker, 1967), these $^{40}\text{Ar}/^{36}\text{Cl}$ values correspond with residence times of 80 and 193 Ma, respectively. Undoubtedly, other factors must be taken into consideration in assigning any significance to $^{40}\text{Ar}/^{36}\text{Cl}$ ratios in fluids, such as incongruent dissolution of K and Cl-bearing phases in rocks and flux of $^{40}\text{Ar}$, from the mantle (e.g., Torgersen et al., 1989). Brines within many sedimentary basins are ultimately derived from surface waters but can have long histories of interaction with rocks (see Hannon, 1987, for review), and although we are not aware of any measurements of noble gases and halogens in a fluid that corresponds precisely with "formation water" in sedimentary basins, this appears to be an appropriate source of some noble gases and salt in some Butte FI. Mixing between several different generations of Br-poor, $^{40}\text{Ar}$-rich brine that ultimately began as air-saturated fresh water and magmatic fluid prior to fluid trapping can account for the measured abundances of noble gases and halogens in the Butte FI studied (Fig. 9).

In the FI assemblages that contain concentrations of $^{36}\text{Ar}$ close to air saturated water ("A" and "B" of Figs. 8, 9), $^{84}\text{Kr}/^{36}\text{Ar}$ varies between slightly less than atmospheric and air-saturated waters (Fig. 10), in general, consistent with an origin of these FI as fresh water, but $^{84}\text{Kr}/^{36}\text{Ar}$ is more variable at Butte than in some other FI that contain $^{84}\text{Kr}$ and $^{36}\text{Ar}$ concentrations equal to air saturated water (Hansoburg, New Mexico, see Böhike and Irwin, 1992c), possibly evidence of different sources of noble gases in the Butte hydrothermal system and/or complex fluid histories. In the one analysis of FI that appear to be of "magmatic" origin, $^{84}\text{Kr}/^{36}\text{Ar}$ is 0.045, outside the range of composition of air-saturated waters and similar to some FI at Bingham, Ascension, and St. Austell.

Sheppard and Taylor (1974) interpreted variations in hydrogen and oxygen isotope ratios associated with Main Stage mineralization at Butte as evidence that "at different times, fluids of vastly different isotopic composition must have been present at essentially the same locations". The data gathered in this study confirm this interpretation and demonstrate that samples of at least three different fluids are trapped in some Butte samples.

$^{40}\text{Ar}/^{36}\text{Ar}$ Age of Hydrothermal Alteration

Gases were extracted from the hydrothermal alteration matrix material adjacent to quartz in sample 322 using the same procedure as in the study of FI. This material contains 2–3 wt% K, no detectable Cl, and yields ages of 56.1 ± 4.1 Ma and 59.7 ± 4.4 Ma. One laser excavation in sample 323 quartz yielded approximately an order of magnitude more K than is typical of Butte FI, probably because the laser sampled mica as well. Correcting for trapped $^{40}\text{Ar}$, using $^{40}\text{Ar}/^{36}\text{Cl}$ of 2.5 $\times$ 10$^{-6}$ results in an apparent age of 56.1 ± 4.2 Ma, consistent with the other dates, but note that this correction factor for $^{40}\text{Ar}$ was arbitrarily chosen. The mean of these ages, 57.3 ± 2.1 Ma, is the same as sericite associated with the "Main Stage" of alteration of 57.9 ± 1.8 Ma (Meyer et al., 1968, recalculated using decay constants of Steiger and Jager, 1977).

ST. AUSTELL, CORNWALL

Background

In the southwest United Kingdom, late Paleozoic granite intrusions are sometimes associated with hydrothermal vein systems containing Sn and Cu, plus Pb- and Li-bearing minerals. The origin of these Cornubian granites and fluids associated with them remains somewhat unclear, with strontium and lead isotope data illustrating some influence of older crust, probably late Proterozoic, in the generation of these.
granites (Hampton and Taylor, 1983), and radioisotopic ages of 295–280 Ma (Halliday, 1980; Hampton and Taylor, 1983; Darbyshire and Shepherd, 1985). Hypotheses for the origin of high temperature FI in the St. Austell granite range from mostly “magmatic” (Bottrell and Yardley, 1988; Böhlke and Irwin, 1992b), to more complex scenarios involving several stages of hydrothermal activity and not necessarily any direct involvement of fluids exsolved from a granitic melt (Alderton and Rankin, 1983). Oxygen and H analyses show that FI in quartz in granites were largely in equilibrium with other phases at magmatic temperatures, with increasing contribution of meteoric water in lower temperature veins (Alderton and Harmon, 1991). Detailed study of Ar, K, and Cl in FI from southwestern England using the neutron-irradiation, noble gas technique demonstrated that mineralized veins containing highly saline FI range between 20–60 Ma younger than the granites (Turner and Bannon, 1992).

The sample studied is a split of the same hand specimen previously studied by Bottrell and Yardley (1988), Böhlke and Irwin (1992b), and Yardley et al. (1992), from St. Meuan Beacon near St. Austell. It consists of quartz + topaz + tourmaline, inferred to have formed at approximately 620°C from aqueous fluids derived from a crystallizing magma (Bottrell and Yardley, 1988), although other workers consider that the FI may be externally derived and represent interaction of fluids with granites at submagmatic temperatures (Manning and Exley, 1984). Halogens and K in FI from St. Austell were measured by LMNGMS in a separate study and the data presented in a previous paper (Böhlke and Irwin, 1992a). Questions about the significance and reproducibility of elemental and gas ratios in the St. Austell FI arose in that study, and two rock chips from the same hand specimen were irradiated along with samples of other “magmatic” systems discussed in this paper.

**Halogens**

Due to the higher neutron fluence and improved calibration of production of Kr and Xe in the 1991 pile-irradiation, these latter data are more accurate and precise than a previous study (Böhlke and Irwin, 1992a), and in this discussion only these latter data are included. In St. Austell FI, Br/Cl is somewhat lower than most of the other FI in magmatic systems studied (between 0.45 × 10⁻¹ and 0.89 × 10⁻³, Fig. 11), with I/Cl typically a factor of ~2 times higher (4.9–12.2 × 10⁻³). The most accurate measurements of halogens in ancient sediments have Br/Cl and I/Cl of 4.4 × 10⁻⁴ and 3.35 × 10⁻⁴, respectively (the median composition of metapelites from Namibia, Boness et al., 1991). Halogen abundances in St. Austell FI could reflect a mixture of magmatic fluids similar to those at Bingham, Ascension and Butte, plus some salts derived from rocks similar to these metapelites. It is not clear at what stage a component of crust may have been incorporated, with possibilities ranging between the melting of the lower crust to addition of fluid from the country rock in the hydrothermal stage. I/Cl and Br/Cl are not well correlated.

**Potassium, Chlorine, and Uranium**

The mean and standard deviation of K/Cl in St. Austell FI determined in this study is 0.147 ± 0.028, slightly higher than the mean K/Cl for leachates from this rock determined by Bottrell and Yardley (1988), of 0.12 ± 0.02. As at Bingham, K/Cl does not correlate with any other variables measured. K/Cl of ~0.15 is consistent with the composition of fluids in equilibrium with K-silicate buffers at temperatures slightly greater than 600°C (Lagache and Weisbrod, 1977), or fluids in equilibrium with quartz monzonite, sulludites, and magnetite at 400–600°C and 0.5–1.0 Kb (Henley et al., 1992).

Uranium occurs heterogeneously distributed in the St. Austell samples, with concentrations in the rock chips analysed in this study ranging up to ~100 ppm by weight, or several orders of magnitude higher if the U occurs entirely in FI. Average concentration of U in St. Austell quartz measured by LMNGMS is 9.1 ppm (by weight).

**Argon, Krypton, and Chlorine**

The first measurements of St. Austell FI using the LMNGMS technique showed large and uncorrelated variations in ⁴⁰Ar/Cl which were difficult to reconcile with the relatively straightforward history inferred for FI in this rock from halogen ratios and other elemental abundances (e.g., Bottrell and Yardley, 1988), hence, a second split of the same sample was irradiated and analysed repeatedly. After subtracting ⁴₀Ar produced by decay of K after trapping, (which is usually 5–10% of total ⁴₀Ar measured), there are at least three components of Ar and perhaps a fourth (Fig. 12): (1) atmospheric contamination, (2) FI having ⁴₀Ar/Cl ~ 1 × 10⁻², and (3) FI having ⁴₀Ar/Cl ~ 1 × 10⁻⁸. There may be a fourth component of Ar in these FI if production of nucleogenic ³⁶Ar is significant. ³⁶Ar is produced by neutron capture from ³⁵Cl(n,γ)³⁶Cl(β)³⁶Ar, a reaction that has a cross-section of 43.6 barns with ³⁵Cl decaying to ³⁶Ar with a half-life of 3.01 × 10⁴ years. Many granites in Cornwall contain high concentrations of radioactive elements, including St. Austell (Allman-Ward, 1985), and these fluids are locally highly saline. ⁴₀Ar/³⁶Ar ratios less than atmospheric are shown by some analyses. It is not clear that these data are accurate enough to establish conclusively this lower-than-atmospheric ⁴₀Ar/³⁶Ar, as there are some limitations of mea-
Fig. 12. 40Ar/36Ar vs. CI/Ar in St. Austell FI. Linear arrays through the composition of "air" usually represent mixtures of air contaminant and gases extracted from FI, indicated by the slope of the mixing line. Radiogenic 40Ar derived from decay of K has been subtracted from all of the data using 40Ar/36Ar = 2.06 x 10^-6 (an age of 280 Ma), although it is usually <1% of total 40Ar. Also shown for comparison are data from a homogenous population of FI from Hansonburg, New Mexico MVT deposit containing concentrations of 36Ar equal to air-saturated fresh water at 20°C, to which was subsequently added in the subsurface 3 molar dissolved CI and 36Ar (Bohike and Irwin, 1992c). Most measurements of Hansonburg are mixtures between an atmospheric component (air contamination) and the composition of CI, indicated by 40Ar/36Ar and CI/Ar furthest from the composition of "air" on this plot. The average CI/Ar in St. Austell FI is much higher than air-saturated fresh waters, probably reflecting the magmatic origin of most of the salts and gases in these FI. Although Cl at St. Austell also contain on average 3 molar Cl, (Bottrell and Yardley, 1988) similar to Hansonburg, they have a much wider range of 36Ar/CI and CI/Ar, which is also typical of most of the other FI of "magmatic" origin studied herein. Variations in CI/Ar are greater than can be explained by just different Cl concentrations in FI. 40Ar/CI is calculated assuming the intercept on the 36Ar/36Ar axis is 250. Note that some of the St. Austell FI have lower-than-atmospheric 40Ar/36Ar, possibly due to the presence of neogenic 36Ar in FI (discussed in text). Data from two separate irradiations are shown (1988 irradiation constants presented in Bohike and Irwin, 1992a,b).

Fig. 13. Abundance of Br and Cl in Ascension Island FI. Linear arrays through the origin indicate constant element ratios. Also shown is composition of modern seawater (Br/CI = 0.0015), which is similar to that of the composition of many mantle-derived basalts (see text).

Explain by any simple processes known to occur in this type of system and there appears to be several different fluids.

**ASCENSION ISLAND**

**Background**

Peralkaline granitic blocks ranging up to several tens of centimeters in diameter occur lying loose on the hillside of the sills of Ascension Island in the middle of the South Atlantic Ocean (Darwin, 1897; Daly, 1925). These blocks appear to have been formed in the subsurface and violently erupted, as they show no evidence of lava coatings. Fluid inclusions are abundant in feldspar and to a lesser degree quartz and amphibole in many of these blocks. In many aspects, these granitic blocks are enigmatic; a detailed description of the petrology, occurrence, and history of previous work on FI in the granitic blocks at Ascension Island is presented in Roedder and Coombs (1967). The composition and distribution of FI in some of these blocks suggest derivation at least in part by exsolution from a magma (Roedder and Coombs, 1967). Oxygen and hydrogen isotopes in lavas and in most of the granitic blocks are similar to other primary, mantle-derived magmas (Sheppard and Harris, 1985). Compared with other ocean basalts, Pb and Sr in lavas are enriched in radiogenic isotopes (Gast et al., 1964; O'Nions et al., 1977; Harris et al., 1982), with 143Nd/144Nd similar to CHUR (reviewed in Faure, 1986).

Study of FI from Ascension Island was motivated mostly by the desire to determine the composition of fluids in igneous rocks removed from any direct contribution from continental crust. The samples studied contain multiple generations of FI and hence, it was hoped that information about processes acting in this magmatic system could be gained from study of FI produced in different stages.

**Halogens**

The mean values of Br/Cl (1.649 ± 0.122 x 10^-3 for sample 133-1 and 1.55 ± 0.224 x 10^-3 for sample 133-4, Table
I; Fig. 13), and variations in this ratio are similar to Bingham Fl and basalts from MORBs and the Azores platform (Unni and Schilling, 1978; Schilling et al., 1980). With the exception of two measurements discussed later, I/Cl ranges between $1.5 \times 10^{-3}$ and $4 \times 10^{-3}$ with an average of $2.37 \pm 0.58 \times 10^{-3}$ (Fig. 14). Variations in Br/Cl and I/Cl are not strongly correlated, although there may be a weak inverse correlation in these ratios in 133-1 and possibly a positive correlation in 133-4. These halogen ratios differ from volcanic gases in the Japan arc (Yoshida et al., 1971), the small dataset for silicic lavas (Becker and Angelier, 1972), and “primitive” mantle nodules (e.g., Jagoutz et al., 1979; Wanke et al., 1984; Wanke and Dreibus, 1988), but are similar to the composition of Fl in mantle xenoliths and diamonds measured using a similar technique (Saxton et al., 1992; Burgess et al., 1993), and not very different from some carbonic-aqueous inclusions in quartz veins from the Italian Alps (Yardley et al., 1993).

The laser was selectively targeted at microscopic areas within elongated, dark grains in the Ascension samples, believed to be amphibole. Replicate analyses of this mineral yield I/Cl more than a factor of two higher than any other studied (Fig. 14). Amphibole in granitic blocks yields 8D of $\sim -50$ to $-55$, which is $\sim 25$ times higher than some lavas, (8D $\sim -80$ for obsidians), and inflow of seawater or meteoric water was proposed as the source of water in these granitic blocks (Sheppard and Harris, 1985; Harris, 1986; Sheppard, 1986). Neither influx of seawater nor meteoric water can explain an increase in I/Cl, but contamination of a magma by pelitic sediments potentially could have this effect, as many fine-grained marine sediments are strongly enriched in I.

Barium, Potassium, and Uranium

Analyses of Ascension samples all include some gas extracted from feldspars or amphibole and do not yield K/Cl ratios of Fl. Average Ba concentrations are $\sim 6$ ppm by weight, with Ba/K $\sim 3.11 \times 10^{-4}$ (atom ratio), similar to feldspars in other granites (see Smith and Brown, 1988). Concentrations of U average $\sim 1$ ppm by weight, which is within the range of concentrations of U in feldspar in many granites (Smith and Brown, 1988), but as pointed out by these authors, U may often occur in inclusions rather than within feldspar crystal lattices.

Argon, Krypton, and Chlorine

Uncorrelated or weakly correlated variations in $^{40}$Ar, Cl, and $^{88}$Kr are present in both samples from Ascension, with the range in $^{40}$Ar/$^{36}$Ar and $^{40}$Ar/Cl similar to St. Austell Fl (see Fig. 12). There are large and uncorrelated variations in ratios of $^{38}$Kr, Cl, and $^{40}$Ar, similar to those noted in Bingham Fl (e.g., Fig. 6).

Tellurium in Bingham, Butte, and St. Austell Fluid Inclusions

Neutron irradiation produces $^{131}$Xe from both $^{130}$Ba and $^{130}$Te by different reactions. In some minerals such as feldspar, pile-produced $^{131}$Xe is dominantly from Ba due to its greater abundance, but this is possibly not true of quartz in a hydrothermal system containing high concentrations of metals and sulfide minerals. Tellurium, Se, and S are “chalcophile” elements with some common chemical properties (see Zingaro and Cooper, 1974; Sindeeva, 1964). If all of the pile-produced $^{131}$Xe measured is from Te, concentrations in quartz from Bingham and Butte are estimated at between $\sim 2$ and $\sim 70$ ppm (by weight) and alteration minerals (“matrix”) adjacent to quartz contain $\sim 2$ to $100$ ppm of Te. It is not clear if Te is sited in some Fl or in microscopic solid inclusions. If dissolved in only some Fl, Te concentrations could be as high as several thousand ppm. Tellurium and Se may be important constituents of Fl that can be measured to a higher degree of precision and accuracy in smaller samples than is possible for S. At Bingham, sample 62-14 contains on average a factor of $\sim 2$. 5 more Te than the other two samples studied, as well as higher Br/Cl and I/Cl, which are all evidence of changes in the chemistry of brines in this system.

In a previous LMNGMS study of Fl (Böhlke and Irwin, 1992a), pile-produced $^{131}$Xe was tentatively attributed to Ba, which yielded Ba/Cl in Fl approximately an order of magnitude greater than analyses of fluids from the Salton Sea and Fl at St. Austell made using other techniques. In view of this more extensive dataset, it is more likely that Te is present in these Fl.

Selenium is also measured in the same Fl (from pile-produced $^{38}$Kr), but at higher detection limits, due to the low abundance of the target nuclide and its low neutron capture cross-section. Selenium was not detected in the Fl analysed in this study, which means that Se concentrations in quartz must be less than $\sim 30$ ppm.

Excess Xenon

Many analyses of Fl have $^{128}$Xe/$^{36}$Ar greater than atmospheric or air-saturated waters (Table 1). Xenon is not correlated with any other parameters measured and its origin remains unclear, as noted in some previous studies of Fl (Böhlke et al., 1989; Irwin and Böhlke, 1991). In analyses that are most air contaminated (deduced from $^{38}$Kr/$^{36}$Ar and $^{40}$Ar/$^{36}$Ar similar to atmospheric), there is a tendency for
trated by FI that have similar halogen ratios but different noble gas isotope abundances and vice versa. Concentrations and ratios of noble gases in most of the FI at Bingham, Ascension and St. Austell are consistent with an unmodified, magmatic origin but some FI associated with magmas (at Butte), originated as air-saturated, low salinity waters and acquired salinity plus some gases subsequently. More comprehensive study of FI from Bingham and Butte is clearly warranted, as variations in halogen and noble gas abundances within and between samples may indicate aspects of the nature of these systems.

Despite their different geologic settings, Br/Cl and I/Cl are similar in FI from Ascension Island, Bingham and some from Butte (Fig. 15). The small dataset for Cl, Br, and I in FI in diamonds and mantle xenoliths (Saxton et al., 1992; Burgess et al., 1993), overlaps with those magmatic FI, implying a common source of salinity. Halogen chemistry of magmas and associated fluids is a little-studied field and it is premature to assign any specific significance to this apparent correlation, but it is worthy of note that all of these analyses of magmatic FI and mantle samples have I/Cl approximately an order of magnitude lower than the composition of “bulk Earth”, implying the existence of a widespread mantle reservoir depleted in I.

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APPENDIX

Descriptions of Samples and Inclusions Studied

All of the samples studied by LNMGMS were prepared by thinning and minimally polishing the remnants of rock chips (the ‘butt-ends remaining after sectioning’), from which petrographic sections had been made previously. Thus, although it was not possible to pre-select specific FI types that were studied petrographically prior to LNMGMS analysis (unlike previous studies), some inferences about the nature of the FI analyzed can be made from adjacent petrographic sections.

Bingham samples

Samples ER63-207a and ER63-208 (abbreviated 207a and 208 hereafter), are from vuggy vein quartz containing sulfide mineralization collected from the north side of close to the bottom of the pit as it was in 1963. Mine coordinates of these samples are approximately 500 W, 1005 at the 5590 level. These two samples were selected from a larger suite of ~10 Bingham samples from the collection studied by Roedder (1971), largely because they contain the most spectacular examples of both the salt-rich FI and very abundant, vapor-rich FI. They contain similar proportions of FIs that appear to be of similar composition, with the principle difference between the two samples being the presence of quartz + Cu sulfides + molybdenite in 208 and just quartz + Cu-sulfide minerals in 207a. Sample 62-14 is slightly different from the others, in that it is from the main body of the porphyry on the East side and the data are mostly from veinlets, “stage 4” (quartz-sericite) which is cut by a “stage 5” veinlet (quartz). Although there is obviously a range of inclusion types in these samples, the most important and convenient categories, in terms of phase volume percentages, are high density, “salt-rich” (liquid + 5–20% solid NaCl), low density “vapor-rich” (liquid + 40–80% vapor, no solids); “vapor” (vapor + 0–20% liquid, no solids); “vapor-rich” (liquid 5–20% vapor, no solids). These categories are used to describe FI in all samples studied. In most areas of all samples from Bingham only a few percent of the total inclusion volume consists of “vapor” or “liquid-rich” inclusions; the major variable is the ratio of the two main types: “salt-rich” and “vapor-rich”. The relative volume ratio of the main inclusion types was estimated petrographically. Counting only those FIs that are large enough to have a significant influence on the data and ignoring two of the four categories (vapor- and liquid-rich FIs, which constitute a few volume percent at most), the volume ratio of salt-rich to vapor-rich ranges between 10:1 to 1:5, with an average of ~1:1. Sample 208 has on average a higher fraction of salt-rich fluid, perhaps as high as 3:1. Analyses of similar volumes within sample 207a and 208 containing similar population densities of FI yield similar abundances of Cl, an indication that the average salinity of FI is not very different in these two samples. Sample 62-14 contains fewer FI, reflected in the smaller amounts of Cl measured in this sample.

Inclusions in 207a appear to be primary, occurring in bands oriented parallel to crystal edges or randomly distributed in the rock matrix, in contrast to the annealed fractures in 207a, 208, and 62-14 are secondary and occur in annealed fractures. In 62-14 FI are smaller and less abundant than in 207a and 208, but appear to be generally similar. Inclusions having a similar range of salinity and filling temperatures to these Bingham FIs have been described in the higher temperature parts of numerous other porphyry copper deposits and some barren intrusions. Within 207a and 208, the nature of FI populations varies widely in individual areas. Salt-rich FI occur intermixed with more vapor-rich FI over a distance of less than 50 μm. This is not always true of vapor-rich-fluor, which can occur in groups without other types. In 207a and 208, groups of relatively large FI are locally large enough and abundant close enough to the surface to be visible and optically targeted through the microscope of the laser microprobe. A typical such group consists of ~5 FIs, each 20–50 μm in diameter. Data from these selected clusters are designated in the complete data Table available from the journal.

Butte samples

The samples studied by LNMGMS are from the Mountain Cave mine, which is ~2000 ft west of the Berkeley pit near the center of the mining district. These samples are referred to as “fresh granite” by mine geologists but are generally altered, as are most of the igneous rocks in this area. ER63-322 is from 4231 High ore vein at 4607 crosscut North, from near ER63-335 of Roedder, (1971), and sample ER63-323 is from A 4655 Lateral West (these sample numbers are abbreviated as 322 and 323 in the text). Sheppard and Taylor (1974), present oxygen and hydrogen isotope data from quartz and sericite in several samples collected in the Mountain Cave mine at the 3,500 and 4,600 levels, possibly close to where these samples are from. Samples 322 and 323 are similar, with the main difference being the degree of alteration. Evolved feldspar phenocrysts in 322 are nearly completely replaced by phyllosilicates, with hydrothermal biotite de-volatilizing locally, associated with sulfide mineralization. Sample 323 still retains some igneous texture, plagioclase twins can still be seen, and hornblende and biotite look relatively fresh, although both are associated with sulfides. Inclusions are very abundant in both samples. Quartz in both samples is dominated by the same two assemblages of secondary fluor that usually occur in planar or curving arrays: (1) equant FI often having the shape of a negative quartz crystal, ranging from less than 1 μm to ~25 μm in diameter, that typically contain ~50% vapor, homogenize at ~400°C, with temperatures of ice melting at close to ~5°C and evidence of a small amount of CO₂ detected by the presence of solid phases (presumably clathrates) at between 0 and 3°C, which indicate a upper limit for salinity of less than 6.5 wt% NaCl, and (2) FI that contain a moderate-sized vapor bubble, typically 5–30% of the FI volume, typically homogenize at ~300°C, with temperatures of ice melting ranging between ~4.6°C and lower than ~6.4°C, indicating an upper limit on salinity of ~8.5 wt% NaCl equivalent, due to the presence of a small amount of CO₂. Sample 322 contains a large proportion of type 1 FI, with local FI assemblages composed of >80% type 1 FI and sample 323 is dominated by type 2 FI that are locally ~80% of the total FI volume. Within both samples, many quartz grains contain mixed populations of these two FI types. The LNMGMS data mostly reflect sampling of these two FI populations, with component “A” derived from the type 2 FI that dominate sample 323 and component “B” from the larger bubble FI that dominate sample 323. Also present within both samples are very rare, irregular shaped FI with a small vapor bubble, which are probably not relevant to interpretation of weathering in this study due to their scarcity. A single quartz grain in sample 322 has the FI assemblage commonly thought of as being of “mag-
matic" origin, with a few FI containing halite daughter minerals and spatially associated vapor-rich FI that have only a small amount of liquid. We believe that the LNMMS analysis of this sample mostly reflects the composition of this assemblage. According to Roberts (1975), FI which represent the fluid which caused the early veining and pervasive alteration have a density of 0.65 and a salinity of ~6 wt% NaCl equivalent, broadly consistent with the character of many of the FI in these samples.

**St. Austell samples**

As in all of the other magmatic rocks studied, FI in these samples are complicated, with variable liquid/vapor ratios and daughter minerals in the same quartz grain. Salinities of FI are variable, but it has been inferred that initially there was a homogeneous parent fluid containing approximately 3 molal Cl (Alderton and Rankin, 1983; Bottrell and Yardley, 1988). Inclusions in the St. Austell sample appear slightly less complex than those in Bingham, also occurring along annealed planar fractures, but with hundreds of FI having visually identical phase ratios in a single plane. Some FI are salt-rich, containing liquid + variable amounts of vapor + halite ± sylvite (~2 ± other small, unidentified birefringent daughter minerals. The majority of FI are vapor-rich, containing a small amount (~25%) of liquid. Some topaz grains contain curving trails of FI that are truncated at the crystal boundary. These FI are distinct from any in quartz, containing ~50% daughter minerals, 50% vapor and no liquid.

**Ascension samples**

Fluid inclusions in two different blocks from the Five Mile Post locality were studied (ER63-133-1 and ER63-133-4, referred to as 133-1 and 133-4 hereafter, equivalent to samples As51.1 and As51.14 of Roedder and Coombs, 1967). These blocks are equigranular, medium grained granites composed of quartz, perthite, aegirine, arvedsonite, acénigmatite, and traces of dalyite, zircon, and pyrochlore. Sample 133-4 is slightly porphyritic. As in the other areas studied, the samples are splits of the remnants of rock chips (the "butt ends"), from which polished petrographic sections were made by Roedder and Coombs, (1967). The samples studied were selected from a larger collection (~10 samples), largely because they contain types of FI interpreted to be of magmatic origin, and are less friable than the others, facilitating sample preparation, irradiation, and handling. Fluid inclusions in these samples are complicated, with four distinct types and three types of "mixtures" of FI types in quartz and feldspar (see Appendix for detailed descriptions of Ascension FI types). Many of the FI in feldspar are primary, with the presence of distinctive FI containing silicate glass, saline solution and gas providing conclusive evidence of magmatic origin. The different types of FI occur intimately intermixed and it is expected that each of the data reflect a mixture between several types. Due to their friable nature and the high population density of FI, it was not possible to thin and polish these samples sufficiently for optical selection of individual FI types. Sample 63-133-1 (also numbered 51.14 in Otago University University collection and 111313.7 in the U.S.N.M. collection) is shown in plate 3, Fig. C and plate 4, Fig. A of Roedder and Coombs (1967); it contains mixed type II + III inclusions. Sample 63-133-4 (also numbered 51.1, 111313.1) is shown in plate 3 b.e of Roedder and Coombs (1967); it contains mixed types I + II and I + III inclusions.

**Types of inclusions in Ascension samples**

1) Silicate glass with small low pressure gas bubble ± dm of fluorite.
2) Water solution with 50-70 wt% halite + other solids, ± large gas bubble containing some CO₂.
3) Dilute water solution and very large, high pressure CO₂ gas bubble. Apparently produced by boiling of type II fluid.
4) Dilute water solution + liquid CO₂ + very large gas bubble.