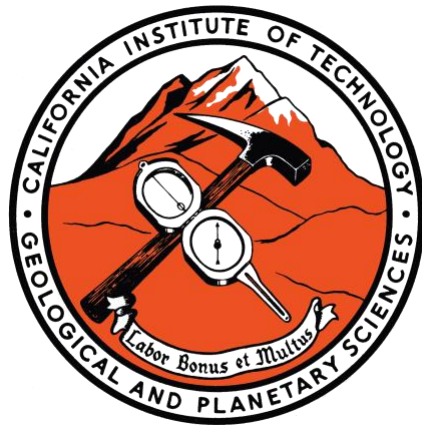


FLUORINATED GRANITIC
MAGMAS: A COMPREHENSIVE
GEOCHEMICAL STUDY

Thesis by

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In Partial Fulfillment of the Requirements for
the degree of
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The discovery of elemental fluorine was a horrific piece of history, as it wounded and killed many of the scientists who attempted to isolate it. It seems fitting that this thesis began during the global pandemic of 2020 and ended with the passing of one of my committee members. I dedicate this work to “that savage beast among the elements” and all those unfortunate souls who choose to study it.

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ABSTRACT

Fluorine, a highly reactive halogen, is understood to be responsible for the unusual behavior of elements in silicic magmas. Rare metals, including economically critical elements like Nb, Ta, and rare-earth elements (REEs), in particular deviate from their expected geochemistry in fluorinated systems, leading to a need to understand fluorine in granitic melts. This work presents many avenues of exploration into the interaction of F and the major, minor, and trace element geochemistry and mineralogy of granites.

Chapter 2 details a method to measure trace elements, including F, by pressing finely-ground powders into a cellulose-bound pellet, then analyzing by X-ray fluorescence (for F) and laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). This method overcomes previous in-house shortcomings by obviating the need to dissolve samples in strong acids, decreasing the dilution effects of fluxing, and removing the possibility of F volatilization during high-temperature fusion.

Chapters 3 and 4 present studies of real granites. Chapter 3 details the results of a global literature review of reported halogens in granitoids around the world, examining trends in whole-rock chemistry with F content and identifying the importance of F on rare metal concentrations by generality. Chapter 4 focuses on two specific rare-metal plutons from the Eastern Desert of Egypt. One of these, Abu Dabbab, is a world-class deposit of Ta, and is interpreted to be an isolated magmatic system that self-metasomatized. The other, Abu Rusheid, is highly enriched in U and REEs, and appears that the mineralization of this pluton occurred over an extended period of time as an open magmatic system.

Chapters 5 and 6 similarly present a compilation and novel study, respectively, of computational, molecular dynamics simulations of fluorinated magmas. The observed preferred F speciations (Al and Si) are not thermodynamically ideal, as the species are not charge neutral, but may be made into a neutral species as AlOF. The F-high field strength species are longer lived, but less common, which F-alkali species are abundant and short-lived.

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O.D.W. participated in conceptualization of the project, all formal analysis, data analysis, and wrote the manuscript

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NOMENCLATURE

Fluorination. The process by which fluorine (F) is introduced to a system, usually involving the substitution of F^- for OH^- in crystal structures or the crystallization of fluorine-bearing phases in interstitial voids.

Granite. A felsic igneous intrusive rock rich in silica and alkalis, composed primarily of feldspar and quartz, with various minor and trace phases

Magmatic Liquid. The liquid from which an igneous rock crystallizes. May refer to *melt* (silicate liquid, unsolidified rock, may be crystal-rich and highly viscous) or *fluid* (hydrous liquid, including water-, CO_2 -, and Cl- rich liquids) or exotic hybrid compositions (i.e., hydrosilicic fluids)

Metasomatism. High temperature ($>300\text{ }^{\circ}C$) fluidic alteration of rock that does not alter mineral textures or compositions enough to consider the rock metamorphosed. Often associated with ore generation.

Mineral. A naturally-occurring crystalline solid with a distinct, defined chemical composition. May be a *major phase* if it makes up a large proportion of the rock (>10 vol. %), a *minor phase* if it makes up a non-negligible amount of the rock ($\sim 1-10$ vol. %), or an *accessory phase* if present in trace quantities (<1 vol. %)

Pluton. A spatially, temporally, and/or compositionally distinct mass of solidified magma. May be composite (multiple episodes of magmatism) or single (one intrusive event)

Speciation. The chemical description of the preferred bonding compound of an element in an open environment.

CHAPTER I

INTRODUCTION

A Brief Description of Fluorine

Fluorine (F) is an element of extremes. It is one of the only elements whose isolation cost multiple scientists their lives, and it may have contributed to the early death of Henri Moissan, who received the Nobel Prize in Chemistry for his work on F. The presentation speech by the Royal Swedish Academy of Sciences in 1906 described fluorine as “that savage beast among the elements,” underscoring its dangerous and dramatic behavior.

It is the most electronegative element, it has the second highest electron affinity (after chlorine), and it has the third highest first ionization energy (after helium and neon) of all the elements in the periodic table (Moore et al., 2010). These traits contribute to the unique geochemical behavior of F, including its extreme reactivity. As a halogen, fluorine does not occur as a native element or pure difluorine naturally, and instead predominantly occurs in ionic compounds. Fluorine is not produced by most fusion processes in stars, causing it to be much less abundant in the universe than the other light elements. Despite only being the 24th most abundant element in the universe (Palme et al., 2014 and references therein), it is the 13th most abundant in the Earth’s crust (Rudnick & Gao, 2014; White 2005). It has a low condensation temperature of ~730 K (~460 °C; Lodders 2003) and is considered highly volatile.

Fluorine is an extremely useful element, and it has been used in steelmaking and ore processing since the 16th century thanks to its ability to lower the melting point during smelting. This trait of helping materials flow led to its name. Unlike other acids, hydrofluoric acid (HF) is able to dissolve glass, leading to industrial applications in etching and laboratory application in the chemical and isotopic analysis of rocks. Synthetic cryolite (Na_3AlF_6) is integral to the refining of aluminum. Fluorine is also widely known for its use in refrigerants, both the ozone-depleting chlorofluorocarbons and their replacement hydrofluorocarbons, and commercial polymers, including polytetrafluoroethylene (Teflon) in non-stick cookware, expanded polytetrafluoroethylene (Gore-Tex) in raingear, and other water-repelling organofluorine molecules (e.g., Scotchgard).

The intersection of human health and fluorine is complicated. It plays no essential role in any metabolic processes, but is an important tool in preventing cavity growth and dental decay. It is a common element in pharmaceutical products, as it improves bioavailability and dosage periods (e.g., Hagmann 2008), and is an important part of selective serotonin reuptake inhibitors (SSRIs). F_2 gas and HF are extremely toxic, but they are very uncommonly encountered outside specific industrial settings. Instead, fluorine-related illness and injury are more commonly related to F consumed as a soluble ion in water, which forms HF in the stomach (e.g., Ozsvath 2009; Ali et al. 2016; Fuge 2019). Prolonged consumption of highly fluorinated water, like water extracted from an aquifer within F-rich rocks, may lead to dental fluorosis and

eventually skeletal fluorosis (Srivastava & Flora, 2020). Most fatal cases of fluoride poisoning in the U.S.A. are from accidental insecticide ingestion. Toothpaste consumption is common and potentially hazardous, especially in young children, but there are very few recorded cases of severe illness or death (e.g., Shulman & Wells, 1997). However, the catastrophic loss of human and animal life in Iceland following the Laki eruption of 1783 is primarily attributed to the large flux of F into the environment (Thordarson & Self, 2003).

Table 1 – Common F-bearing minerals and their formulas

Common Halides and Oxides	Formula	Common Micas and Amphiboles	Formula
Fluorite	CaF_2	Fluorannite	$\text{KFe}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$
Cryolite	Na_3AlF_6	Fluorophlogopite	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$
Fluocerite	$(\text{La,Ce,Nd})\text{F}_3$	Polyolithionite	$\text{KLi}_2\text{AlSi}_4\text{O}_{10}(\text{F,OH})_2$
Topaz	$\text{Al}_2\text{SiO}_4(\text{F,OH})_2$	Trilithionite	$\text{KLi}_{1.5}\text{Al}_{2.5}\text{Si}_3\text{O}_{10}(\text{F,OH})_2$
Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	Fluoroedenite	$\text{NaCa}_2\text{Mg}_5\text{Si}_7\text{AlO}_{22}\text{F}_2$
Amblygonite	$\text{LiAl}(\text{PO}_4)\text{F}$	Fluoropargasite	$\text{NaCa}_2\text{Mg}_4\text{Si}_6\text{Al}_3\text{O}_{22}\text{F}_2$
Bastnaesite-(La,Ce)	$(\text{La,Ce})(\text{CO}_3)\text{F}$	Fluorotremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$

In geochemistry, fluorine is considered to be a highly volatile lithophile element (McDonough & Sun, 1995) and is often observed to be concentrated in granites and granite-affiliated ore deposits. It is fluid-mobile, although it will preferentially partition into melt relative to fluid (e.g., Manning, 1981; Webster & Holloway, 1990), and it is incompatible in most anhydrous major minerals, like feldspars. Representative phases that contain stoichiometric fluorine are presented in Table 1. There are notable complications when attempting to measure the F content of rocks and minerals. Due to its high ionization potential, it cannot be analyzed by plasma-source mass spectrometry under most conditions. It has one characteristic X-ray with a low energy (677 eV) whose measurement by X-ray spectroscopy (i.e., X-Ray Fluorescence [XRF] spectroscopy or electron-beam instruments), requires special diffracting crystals, thin windows, and careful corrections for overlap with the Fe and Mn $L\alpha$ X-rays at 704 and 637, respectively. It may be volatilized during high-temperature sample preparation methods like fusion, and mineral or whole-rock dissolution methods that use HF are obviously unsuitable for quantitative analysis of F concentrations.

It should be noted that the global fluorine cycle is poorly understood, as several major fluxes and reservoirs are not constrained quantitatively. The global ocean has

Fluorine in Granitic Melts

Granites are an intrusive igneous rock type rich in silica, made up primarily of quartz, feldspars, and mica and/or amphibole. In some cases, they are interpreted to be the

slowly cooled residual melt from the fractionation of a large body of primary magma and in others, they are viewed as the partial melt of other rocks (e.g., Moyen et al., 2021). Due to their high silica content, these melts are extremely viscous and, when combined with the high content of crystals, behave more like a “mush” than a true liquid, introducing complications when examining their geophysical properties. Regardless of formation mechanism, they are enriched in elements that are considered incompatible (i.e., elements that do not fit into common mineral structures), including fluorine.

There are many ways to classify granites including: major mineralogy (e.g., syenogranite versus monzogranite); accessory mineralogy (e.g., two-mica granite); effective color (e.g., leucogranite); petrogenetic type (e.g., I-type or S-type; Chappell and White, 1974); tectonic environment (e.g., anorogenic or synorogenic granite); and more. A particularly unusual category of granite is the poorly defined “rare-metal” granite, which host significantly elevated concentrations of trace elements (i.e., Nb), and are viewed as important reservoirs of critical metals (e.g., Küster 2009). One variant of rare-metal granite is the “radioactive” granite, noted for its elevated U and Th content.

Critical minerals are defined as natural materials that are vital to either the economy or military capability of nations and are also susceptible to supply disruption (U.S. DOE Energy Act of 2020). F and fluorspar (fluorite) are considered critical. Many other chemical elements are also critical minerals, including Li, Be, Ga, Sn, Zr, Hf,

Nb, Ta, and rare-earth elements (REEs; the lanthanides $\pm$ Y and Sc). All of these are frequently enriched in granites thanks to their generally incompatible nature (Figure 1.1). Several of these, namely Zr, Hf, Nb, and Ta, are considered high field strength elements (HFSEs) because they have high ionic charges (+4 for Zr and Hf; +5 for Nb and Ta) and relatively small ionic radii (~ 0.7 Å). REEs have moderately high charges (+3) and moderate ionic radii (~ 0.9 - 1.2 Å), and are broadly electropositive. Both HFSEs and REEs are insoluble in aqueous fluids, unless there are ligands like F.

This work presented in this dissertation represents multiple avenues of investigation into the behavior of fluorine in granitic melts, and its relationship to the enrichment and mobility of rare metals. This will take place across multiple scales, including a global review of granites, a highly detailed study of the geochemistry and mineralogy of two specific plutons, and computer simulations of the atomic interactions in a silicate melt.

Chapter 2 presents a novel method for the analysis of whole-rock trace elements, including F and Cl, in geologic samples. This method utilizes powder pellets, bound with cellulose and pressed in a vacuum press, ablated in a laser-ablation inductively-coupled plasma mass spectrometer (LA-ICP-MS) for most elements and analyzed by X-ray fluorescence (XRF) for the halogens. Unlike previous in-house methods, this method prevents volatile loss by circumventing high-temperature sample preparation techniques and minimizes dilution of trace elements, as well as avoiding the need to use the hazardous acid HF.

Chapter 3 is a review of previously published whole-rock fluorine data for granitoids on a global scale. The major reviews of this topic have previously focused on a small number of publications, so the approach here was to compile all works. In total, this compilation includes over 280 papers, representing 78 countries and territories, and contains more than 4000 individual analyses. The whole-rock geochemistry trends with fluorine in some ways are not surprising, as it correlates with other fluid-mobile, incompatible elements (e.g., Li & Rb). The correlation of F with HFSEs is complicated, with several elements splitting at high F concentration into a peralkaline, ionic charge and radii controlled (CHARAC) population and a peraluminous, sub-CHARAC population.

However, previous assertions about global trends between granitic type and fluorine content are not as globally valid as believed, as the range of F concentrations is the same in A-, I-, and S-type granitoids. Although A-types are slightly more fluorinated than the other types, the difference in median F is not statistically significant. Similarly, granites containing both mica and amphibole generally have less F than rocks contain just mica or amphibole.

Chapter 4 is a highly detailed study of two rare metal granites from the Eastern Desert of Egypt named Abu Rusheid and Abu Dabbab. Abu Rusheid is a highly altered – and highly fluorinated – heterogeneous rare metal granite, particularly enriched in uranium, REEs, and HFSEs. Abu Dabbab is a much smaller pluton, but is one of the

best reserves of Ta and Hf in the world, and between the beginning and conclusion of this project, it has become an active mine.

The work on these plutons includes: whole-rock geochemistry, including data collected using the method developed in Chapter 2; mineralogy; mineral chemistry determined by electron probe microanalysis (EPMA) and scanning electrode microscopy (SEM). Select additional methods – electron back-scatter diffraction (EBSD) and Raman spectroscopy – were employed to investigate accessory phases, including potentially novel minerals.

Chapters 5 and 6 are the results of molecular dynamics simulations of fluorinated silicic melts, including a review of previously reported parameters and forms of the force-field equation (Chapter 5) and the results of the simulations (Chapter 6). Ab initio calculations, although more accurate, are limited in their temporal and spatial scope, and so to accurately reproduce magmatic systems, the interatomic potential equation was calibrated on ab initio calculations. This potential can then be applied to larger systems of atoms and longer simulation times than can practically be computed *ab initio*.

The periodic table is color-coded to highlight specific geochemical groups. The legend below the table defines these groups:

Y	Rare-Earth Elements	Cs	Large Ion Lithophiles	Si	Major elements in the crust	F	Halogens
Zr	High Field Strength Elements	Ir	Platinum-Group Elements	V	Other Transition metals	B	Other elements
U	Hybrid REE/HFSE	Li	Other "rare metals"	Kr	Noble Gases	Tc	Unstable & extinct elements

The periodic table itself shows the following elements and their groupings:

- Group 1:** H, Li, Na, K, Rb, Cs, Fr
- Group 2:** Be, Mg, Ca, Sr, Ba, Ra
- Group 3:** Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
- Group 4:** Ti, Zr, Hf, Ta, Nb, Mo, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn
- Group 5:** V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 6:** Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 7:** Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 8:** Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 9:** Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 10:** Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 11:** Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Group 12:** Zn, Ga, Ge, As, Se, Br, Kr
- Group 13:** B, Al, Ga, In, Tl, Pb, Bi, Po, At, Rn
- Group 14:** C, Si, Ge, Sn, Pb, Bi, Po, At, Rn
- Group 15:** N, P, As, Sb, Te, I, Xe
- Group 16:** O, S, Se, Te, I, Xe
- Group 17:** F, Cl, Br, I, Xe
- Group 18:** He, Ne, Ar, Kr, Xe, Rn

Additional annotations include a starburst around Fluorine (F) and a grey box labeled "Transuranic Super-Heavy elements" below the main table. The actinide series (Ac, Th, Pa, U) is shown below the lanthanide series, with a grey box labeled "Transuranic Actinide elements" below it.

[Figure 1.1](#) – A geochemist's annotated periodic table.

A periodic table emphasizing the geochemical groupings that will be used in this work (White 2005).

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CHAPTER II

LASER ABLATION OF SILICATE ROCK PRESSED POWDERS AS AN EFFICIENT TRACE-ELEMENT ANALYSIS METHOD

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Abstract

Whole-rock powder pressed pellets analyzed by LA-ICP-MS offer an alternative to whole-rock powder or lithium borate fused bead dissolution methods for trace element analysis. In addition to reducing the need to use strong acids and pressurized bombs, powder pellets offer the opportunity to quantify Li and trace elements with minimal dilution. Previous work in this area has emphasized spot analyses, achieving sufficient sample homogeneity through wet-grinding of powders to nanoparticulate sizes. Here, we demonstrate that using a larger laser spot size and line-scan analyses reduces the restriction to moderate particle sizes ($\leq 100 \mu\text{m}$). We present data for 58 major and trace element analytes collected from 27 USGS and GSJ geologic reference materials prepared with this method. The majority of elements are measured accurately; we identify the few elements that are exceptions and do not yield reliable results with this method.

Introduction

Whole rock major and trace element concentrations are the basis for geochemical classification of rocks, for petrogenetic models of rock-forming processes, and for geochemical prospecting for ore deposits. Rocks are heterogeneous assemblages of minerals, so whole-rock analysis necessarily requires some homogenization or averaging process, applied at a suitable scale relative to the grain size. Typically, whole rock analyses are conducted via high-temperature dissolution of rock powders into a flux, usually lithium metaborate and/or tetraborate, whereby fusion efficiently dissolves silicate phases and the resulting quenched glass is homogeneous

(Ingamells, 1970; Cremer and Schlocker, 1976; Pinto et al., 2012; Feldman, 1983). The glass beads or “pills” produced via this method are then analyzed via X-ray fluorescence (XRF) spectrometry or inductively-coupled plasma optical emission spectrometry (ICP-OES) for major and minor elements. Although trace elements can be analyzed, commercially available XRF spectrometers typically have a lower limit of detection of $\sim 1 \mu\text{g/g}$. Thus, if a bead is made with a 1:5 or 1:10 ratio of rock sample to flux, the nominal detection limit for the concentration of an element cannot be better than 5 or 10 $\mu\text{g/g}$ (Ingamells, 1970; Feldman, 1983), respectively. Thus, to obtain a full suite of trace element analyses, typically a second analytical method is required.

Trace element analyses can be performed on samples prepared as glass beads, either by dissolution in acids and subsequent analysis by inductively-coupled plasma mass spectrometry (ICP-MS; e.g., Cremer and Schlocker, 1976; Feldman, 1983; Yu et al., 2001), or by laser ablation ICP-MS (LA-ICP-MS) of the fused material (e.g., Eggins, 2003; Yu et al., 2003). However, there are limitations to this method. By the nature of the lithium borate fluxes used, these methods are not able to measure Li or B. Moderately volatile elements may be lost during flux fusion and the diluted nature of the bead decreases the analytical sensitivity of low-concentration elements. Alternatively, sample powders may be dissolved in acids directly, although this approach must address the silicates (e.g., zircon) and other minerals (e.g., chromites, phosphates, etc.) that are notably resistant to acid dissolution, requiring hazardous

chemicals, heat, and pressurized vessels, such as Parr bombs (Takei et al., 2001; Révillon and Hureau-Mazaudier, 2009; Yu et al., 2000) or microwave digestion techniques (Balaram, 1997).

Another method, more commonly used with XRF major and minor elemental analyses, is the creation of powder pellets. Such pellets are mixed with a binder, commonly cellulose or wax, and pressed in die presses, with or without vacuum. This method has the advantage of limited sample dilution, as only a tenth to a fifth of the pellet mass is binder. Powder pellets also have the benefit of limited loss of volatiles, allowing for measurements of halogens (Krishna et al., 2012), unlike fusion and acid dilution methods.

Analysis of trace elements in pressed powder pellets by LA-ICP-MS has been described and applied in a limited capacity (Gray, 1985; Garbe-Schönberg and Müller, 2014; Mukherjee et al., 2014; Van Heuzen and Morsink, 1991; Guldris Leon et al., 2022). If this method can be executed efficiently for whole-rock trace element analysis, there would be several advantages over dissolution ICP-MS methods. First, the elements that can be measured with pellets include most of the periodic table, with very few exceptions. Halogens, phosphorus, and sulfur are restricted to XRF. Major elements are also better measured by XRF but could be included in a LA-ICP-MS protocol. The elements measured are highly customizable to different lab requirements or research interests, and may include Li and B. Second, this method would be significantly safer, as dissolution methods necessitate significant volumes

of concentrated hydrofluoric acid, an infamously hazardous chemical, and powder dissolutions are only successful when performed in heated and pressurized vessels (Révillon and Hureau-Mazaudier, 2009). Finally, this method is accessible to many labs at relatively low cost. Instead of a separate preparation for each analytical method, each preparation costing \$40-100 per sample at larger facilities, multiple whole-rock methods (XRF, ICP-MS) may be employed on a single pellet produced with cellulose, a cheap and readily available compound. This preparation of pellets requires simple equipment and materials and may use any die set, vacuum pump, and hydraulic press that achieves the needed pressure, reducing the need for specialized equipment for laboratories with budget limitations.

However, a primary concern noted in previous studies that developed protocols for LA-ICP-MS on pressed pellets was minimizing the size of particles pressed into a pellet in order to achieve homogeneity and eliminate nugget sampling effects. As a result, researchers have dedicated much of their effort to ensuring the median grain size was below a recommended threshold, generally nano-particle size ($d_{50} \leq 1.5 \mu\text{m}$; Garbe-Schönberg and Müller, 2014). Achieving such fine particle size can itself be a slow and difficult preparation step, as well as a potential dust inhalation hazard, but has been recommended to improve homogeneity. Here we explore the potential to analyze whole-rock trace elements via LA-ICP-MS of pressed powder pellets for a wide variety of geologic materials for sample powders ground by routine methods to $\leq 100 \mu\text{m}$. Our method eases the strict particle size requirements, allowing LA-ICP-

MS analyses on pressed pellets to be accomplished efficiently and inexpensively for whole-rock trace element analysis.

Experimental Methods

Materials

Sample preparation procedures were initially evaluated using an in-house reference material (SNB-16-2), as the trial-and-error process necessitated sacrificing many grams of sample. Once the conditions of pellet cohesion were satisfactory, a suite of 29 publicly available geochemical reference materials from the United States Geological Survey and the Geological Survey of Japan were made into pellets. These reference materials, in addition to the in-house standard, were used to determine the optimal conditions for the laser. LA-ICP-MS drift correction and additional tuning relied on standard glasses from NIST (SRM 610, 612, 614, and 616) and Corning (95IRV, 95IRW, 95IRX). The full list of materials and the range of concentrations is presented in Supplementary Table 2.1. Reference materials with preferred values (GEOREM; Jochum et al., 2005), certified values, or those that have been used in GeoPT inter-laboratory studies are noted.

Most rocks contain sufficient silicon that silicon is an obvious choice to use as an internal standard. However, there are rock types that are naturally low in or free from silicon, such as carbonates, phosphorites, and some ore bodies. A few of the reference materials used (NOD-P-1 and NOD-A-1) are oceanic manganese nodules with 14

and 4 wt. % SiO₂, respectively. To adequately analyze these and similar unknowns, additional testing was necessary.

Sample preparation

To evaluate a powder-pellet method, the following variables were considered during sample preparation: 1) ratio of sample to binder and effect on pellet cohesion, 2) effect of sample mass on pellet cohesion, 3) effect of pressing under a vacuum, and 4) effect of pressure and dwell time. In this section we describe the final optimized methodology. The results of varying these preparation parameters are described below in the discussion.

The only binder tested was cellulose. Whole rock powders prepared in-house were ground in either a ball mill (Retsch PM 200, with agate or corundum grinding vessel and spheres) or a shatter box (with alumina grinding vessel and puck), while reference material powders were used as sold, with no additional milling. Powders were weighed and then sieved with the cellulose binder through multiple grades of mesh. Particles too large for each sieve were ground by hand with a corundum mortar and pestle and sieved again. Corundum was used instead of the more common agate due to the presence of some hard phases, such as zircon (H=8.5) and spinel (H=8-8.5). All particles had a final size less than 106 μm (mesh no. 140), as determined by sieve size.

Pellets were produced with a diameter of 13 mm. This size balanced the ability to fit multiple small samples in the laser ablation chamber (section 2.3; Figure 2.1), while still being large enough to measure select major elements, halogens, and S on the same pellet by XRF. With this size of pellet, nine samples could be loaded together in the ablation chamber (Fig. 2.1). We tested binder-sample ratios from 1:4 to 1:9 and ultimately settled on a binder-sample ratio of 1:5 with a total mass of 400 mg to create a consistent sample thickness of ~1 mm. For pressing the pellet, several discrete applied loads, ranging from 7 to 8.5 tonnes, were tested with and without vacuum for various dwell times. In our final protocol, pellets were pressed under vacuum at 8.1 tonnes (18,000 pounds) for 30 seconds.

LA-ICP-MS analytical conditions

Experiments were designed to optimize the following analytical parameters (1) line or spot analyses and number of replicates; (2) effect of aperture size; (3) effect of frequency and power; and (4) the choice of internal standard, ^{27}Al , ^{28}Si , or ^{29}Si . Here we describe the final methodology used; in the discussion below, we describe our decision making to arrive at this final method.

All measurements used an UP-193 laser ablation system from New Wave Research (c. 2007), equipped with the Supercell ablation chamber, and coupled to an Agilent 8800 Triple-Quad ICP-MS operated in no-gas single-quad mode with Ar carrier gas. Samples were loaded in a 3-D printed PLA holder with NIST 610 and 612 glass standards and inserted into the chamber (Fig. 2.1a). Operating conditions for the ICP-

MS can be found in Supplementary Table 2.2. The laser was warmed up for at least 30 minutes, until negligible variation in the reported fluence, then tuned at the beginning of each session. The sample chamber was purged until counts on specific masses corresponding to CO_2^+ , N_2^+ , and $^{27}\text{Al}^+$ had stabilized. Spots and lines were located and programmed using the New Wave Research program. Before each analysis, the laser was fired at the closed shutter for 15 seconds to both warm up the laser and establish a background-count rate for each line. Pressed pellets were then ablated via line analyses with a 120 μm spot size at a frequency of 10 Hz at 80% laser power. A 500 μm line was analyzed at a scan rate of 10 $\mu\text{m}/\text{s}$, resulting in 50 seconds of total ablation time. After each analysis a 60 second washout period was included. Calibration was achieved by measuring replicates of two reference materials at the beginning of each batch, collecting 5 lines on each (see Choice of Calibration). Samples were analyzed 7 times and between samples, NIST SRM 610 was analyzed between samples as the quality control (QC) to monitor drift during the batch. Additional glasses from NIST (SRM 614, 616) and Corning (95IRV, 95IRW, 95IRX) were measured during sessions for reproducibility and in the derivation of detection limits [Supplementary Table 2.1].

Due to the complexity of natural samples, 58 analytes were selected from lithium (mass 7) to uranium (mass 238), including 10 major elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) and 43 trace elements (Li, Be, B, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Ag, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,

Tm, Yb, Lu, Hf, Ta, W, Pb, Bi, Th, U). Si was analyzed on two masses, using ^{28}Si as the reference internal standard for all unknowns. Ca and Pb were analyzed on two and three masses, respectively. A few sessions analyzed multiple isotopes of Cr and W for isobaric interference testing. All other elements were analyzed on the single mass recommended by Agilent Technologies [Supplementary Table 2.1a]. This list of analytes includes elements found in phases known to be resistant to grinding, such as Zr and Hf in zircon (Feldman, 1983; Garbe-Schönberg and Müller, 2014), as well as elements that are challenging to ionize, including B and As. Two major elements, K and P, were measured without the expectation of quantitative results.

The Agilent Mass Hunter software was used to set integration intervals for each analyzed spot, make background corrections, and implement the calibration with two reference materials (BHVO-2 and STM-1) using ^{28}Si as an internal standard (ISTD).

Details of the XRF calibration and analytical conditions are presented in the supplementary text and Supplementary Table 2.3.

Results and Discussion

Effects of sample preparation on pellet quality

Satisfactory cohesion of a pressed pellet was determined by its ability to withstand a drop test (i.e., it does not break when dropped from a height of ~30 cm). This was attained when the ratio of binder to sample was 1:4 or 1:5. When the ratio was 1:7 or 1:9, the commonly recommended ratio for 40 mm pellets, samples this size did not pass the drop test (Fig. 2.2a). We proceeded with a binder-sample ratio of 1:5 to

minimize dilution effects from the binder. Sample mass had a minor effect on the cohesion of the pellet, however pellets that were too thin frequently broke in removal from the press. Between 300 and 800 mg, samples were cohesive. We elected to use a total mass of 400 mg to create a consistent pellet thickness of ~1 mm. The Si-poor samples mentioned above were most accurately analyzed when combined with a small amount of lab-grade SiO₂. These materials were weighed out to 264 mg, combined with 66 mg of SiO₂ and 70 mg of cellulose to maintain the sample-binder ratio.

Pressing under a vacuum did not impact pellet cohesion during a drop test, but did improve cohesion under the laser. Samples pressed under vacuum displayed fewer loose particles that could be ‘dislodged’ during ablation. (Fig. 2.2b). All pellets were therefore pressed under vacuum. Several discrete applied loads between 7 and 8.5 tonnes were tested, though there was little effect on the pellet quality. We therefore elected to proceed with 8.1 tonnes (18,000 pounds), the manufacturer recommendation for making KBr pellets in the 13 mm die. Similarly, no effect was observed with prolonged ‘dwell time’, or duration at peak pressure. Regardless of the time at pressure, samples were released from the applied load at a manually moderated rate.

In conclusion, the ratio of binder to sample had the most significant effect on the quality and durability of the produced pellets.

Effects of analytical conditions

We elected to use the maximum aperture available in our ablation system (120 μm) to maximize the surface area analyzed. This also allowed us to maximize the number of ions produced and to avoid running into particles similar in diameter to the laser, which was observed to decrease precision. Samples were analyzed at a laser repetition rate of 10 Hz. Laser powers between 50 and 90% were evaluated, with resulting counts consistent between lines for powers at or above 80% ([Supp. Fig. 2.1a](#)). Samples were subsequently analyzed at 80% laser power, resulting in a reported fluence of 1.21 J/cm² and an irradiance of 0.44 GW/cm². Lines were generally preferable to spots because of their ability to mitigate any nugget effects. Line lengths of 300, 400, 500, 750, and 1000 μm were tested (Fig. 2.3). Longer lines sample more of the surface area at the cost of a longer time per sample for a given stage motion rate. There was a negligible return in improvement of signal variability above 400 μm line length. At and above 500 μm line length (Fig. 2.3b), there was also satisfactory agreement in the total counts for each element between different line replicates. This can be interpreted as the approximate length-scale at which nugget effects are present in the reference materials. We cannot prove that this protocol overcomes all possible nugget effects in all natural materials, but additional monitoring of the temporal stability of the count rate as the line scan is conducted can detect the presence of small, highly enriched grains.

We also tested different scan rates, number of passes, and the side of the pellet (i.e., top or bottom when removed from the press). The scan rate did not impact signal stability and we ultimately selected a scan rate of 10 $\mu\text{m/s}$, which resulted in 50 seconds of signal production (Fig. 2.3b). The homogeneity of the sample was evident in the lack of variation between the “top” and “bottom” sides of the pellet. We did occasionally encounter materials with very poor cohesion; these could be made into acceptable pellets by adding a layer of pure cellulose on one side and evidently it was then necessary to analyze the opposite side. There was limited variation between single and multiple passes on the same line, except for volatile elements, like Na, which decreased between the initial and subsequent passes. An acceptable precision for an element, as determined by a standard error of the mean below 10% rel., was generally obtained with 5-10 line analyses (Supp. Fig. 2.1b), with longer lines requiring fewer analyses. Coarser grained rocks (e.g., GSP-2) required more lines than others for comparable precision, generally 7-10 lines. For the final analytical protocol, we collected seven 500 μm line analyses of a sample, as this balances efficiency and acceptable precision, followed by NIST SRM 610 as a QC to monitor drift in signal throughout the sequence. Altogether, the analytical protocol requires a total of 14 minutes of analysis per sample with an ablated surface area of about 420,000 μm^2 , a little less than 0.5% of the available surface area of the pellet.

Choice of calibration and internal standards

Initial tests run with a calibration based solely on NIST SRM 612 were satisfactory for some elements, but there is a large mismatch between concentrations of some major elements in typical rocks and their concentration in this reference material (see Elements of Note). Mounts were then made of NIST SRM 610, which has higher concentrations of many of all trace elements. There were also concerns about the matrix effects of calibrating on a glass and analyzing a powder pellet. To combat this, the large suite of reference materials was analyzed with two-glass calibrations and evaluated a “correction factor” was evaluated in the style of Garbe-Schönberg and Müller (2014). However, we observed that instead of using the glasses and an observational correction that must be calculated every session, we obtained the same level of precision when calibrating directly on just two reference materials (BHVO-2 and STM-1). Hence, all data presented here were calibrated on two reference materials. Use of a USGS natural reference glass (e.g., BIR-1g) might also be appropriate, but none were available for use during testing of this method. The glass standard, NIST SRM 610, was used only as the QC in data collection runs.

When used as the ISTD, ^{27}Al , ^{28}Si , and ^{29}Si generally produced results within error of each other in the samples. ^{28}Si has a significant isobaric polyatomic interference with $^{14}\text{N}_2$, but this was accommodated by monitoring background counts on mass 28. Analytical runs were not begun until the background was flat, with variations less than 0.6% over 3 minutes. The signal to background ratio of ^{28}Si to $^{14}\text{N}_2$ is at least 15, provided the sample has a minimum SiO_2 content of ~10 wt.%. Rocks with less

SiO₂ than this were mixed with a known mass of SiO₂ during pellet preparation and corrected following analysis. Background counts on 27 (Al) and 29 (Si) were lower, but much less regular and did not level out with extended instrument warm-up. Ultimately, ²⁸Si provided the most replicable results and was used as the ISTD.

Post-processing

Some of the data processing was completed in the Agilent software, including calibration and referencing to ISTD values for the samples, determined by XRF. Due to limitations in the software used to acquire the data, additional processing routines were implemented with Python scripts. These were used to evaluate the signal-to-noise of each acquisition, the variability within each sample, and the appropriate limits of detection and quantitation for each element. A script was prepared to evaluate drift of the QC measurements and perform a drift correction, but none of the analytical runs we performed experienced significant drift.

Method validity for geochemical reference materials

The various methods trials described above were successful in quantifying the majority of the 58 analytes within error (5-10%) of the preferred values reported by GEOREM (Jochum et al., 2005) for each reference material not used in the calibration. The exceptions are generally present in elements with low concentrations or those that experience analytical complications (see Elements of Note). Samples of reference materials that do not have preferred or certified values yielded concentrations in a similar range to those previously reported. The plots shown in

[Fig. 2.4](#) show the average value measured, normalized by the accepted values from GEOREM (Jochum et al., 2005).

Despite the concerns expressed in previous works (Garbe-Schönberg and Müller, 2014; Wu et al., 2018), the size of the particles within the pellet did not prove to be a severe complication. Provided the particle sizes were all less than the diameter of the beam, long ablation lines ($\geq 500 \mu\text{m}$) and sufficient replicates (at least 5-7) were able to quantify elements of concern with replicable accuracy. Due to the issues these papers reported, we specifically examined the variations in signal of Zr, which is dominantly hosted in zircon, a hard mineral that can be difficult to grind to an acceptable size. We observed Zr spikes in the ablation lines, but they were uniformly distributed across the sample such that the lines all quantitatively record the same concentration and, based on the reference materials, this is the correct concentration (Fig. 2.4).

Finally, with long analytical runs, a drift correction may be necessary. However, each batch of pellets and standards takes about 2.5 hours and the observed drift in QC concentrations was negligible, rendering a drift correction unnecessary (Supp. Fig. 1c). Compared to previous in-house trace element protocols, LA-ICP-MS of pellets is more accurate for more elements ([Supp. Fig. 2.2](#)).

Elements of Note

Although most elements (42 of 53) could be measured accurately to within 10% of reference values, the concentrations of several elements proved difficult to robustly quantify. ^{52}Cr was irregular in most samples, an issue consistently reported in previous works (Garbe-Schönberg and Müller, 2014; Mukherjee et al., 2014; Wu et al., 2018; Zhang et al., 2016). This issue arises from argon-carbides forming between the carbon-rich cellulose binder and the carrier gas. It was confirmed by analyses of cellulose blanks, in which “Cr” contents of around 1000 $\mu\text{g/g}$ were reported by LA-ICP-MS, but ≤ 6.0 $\mu\text{g/g}$ by XRF, as well as by comparing concentrations derived from masses 52 and 53.

All previous studies also report issues with measurements of Pb, which exhibited irregularities only in our standard glasses and not in our pellets, and Zn, discussed below. Additional elements previously reported to be inaccurate when measured via laser ablation of pressed powders include Rb and Cs (Wu et al., 2018; Zhang et al., 2016), Hf (Garbe-Schönberg and Müller, 2014; Mukherjee et al., 2014), and U (Garbe-Schönberg and Müller, 2014; Zhang et al., 2016), though none of these elements posed issues with our method.

Elements like Be, B, P, Zn, and As are difficult to ionize, with ionization efficiencies lower than 75% (Houk, 1986). Despite this, Be had close to zero background counts and could be measured accurately and precisely in reference materials. The other elements, however, were frequently within an order of magnitude of the background. B specifically demonstrated an anomalously high background, which is most likely

an artefact specific to our ICP-MS instrument because it has been extensively used to analyze borate bead dissolutions. This reasoning was supported by the marked decrease in the background count rate of both Li and B observed with the use of new sample and skimmer cones. Unfortunately, the background counts on B were still too high to satisfactorily quantify the concentrations in most reference materials. P was included as an exercise to qualitatively trace rare-earth nugget effects due to phosphates (e.g., monazite), analogously to Zr in zircon, but concentrations of P are more accurately obtained via XRF.

All first-row transition metals were analyzed by this method. However, the prevalence of polyatomic isobaric interferences (e.g., $^{40}\text{Ar}^{12}\text{C}^+$ and $^{52}\text{Cr}^+$; $^{40}\text{Ar}^{16}\text{O}^+$ and $^{56}\text{Fe}^+$) and poor ionization yields (e.g., Zn) means some of the concentrations measured are inconsistent with established values. Furthermore, there are potential contaminations by the metal sieves and press housing (e.g., Ni, Cu), interpreted from infrequent spikes in the time-series, that affect the calculated concentrations. Fortunately, all elements with issues in this method can be measured adequately by XRF.

Method shortcomings

A number of elements could not be measured precisely and accurately. The background counts of ^{11}B on this instrument are too high to allow for measurement in most geologic materials, corresponding to limits of detection around 22 $\mu\text{g/g}$. ^{75}As experience poor ionization yields, as mentioned above, in addition to a high

background. These elements are susceptible to being caught in the gas phase, as opposed to the aerosol phase, and are therefore biased in transport (Kuhn et al., 2003). ^{107}Ag had the worst performance in the geologic pellets. The poor accuracy is challenging to explain. It is not due to interference by $^{91}\text{Zr}^{16}\text{O}^+$ ([Supp. Fig. 2.3a](#)), nor is it due to a high background, cellulose contamination, or calibration issues. Instead, both the low precision and accuracy are most likely due to the counting statistics of small numbers, as the highest concentration ($0.105\text{ }\mu\text{g/g}$ in RGM-2) corresponded to 110 counts on mass 107. Similar issues may be to blame for the poor performance of Mo and Bi. W was higher than accepted values in samples of multiple lithologies, both in reference materials and those prepared in-house. This discrepancy was not uniform and was not present in all reference materials. Additional testing on multiple isotopes of W (^{182}W , ^{183}W , and ^{184}W) yielded mutually coherent behavior that was independent of Er (oxide), Nd (argide), or Yb (carbide) concentrations; this observation supports contamination by W itself, rather than polyatomic interferences. However, a high concentration from the cellulose blank ($\sim 140\text{ }\mu\text{g/g}$) that broadly correlates with mass 52 ([Supp. Fig. 2.4](#)) and is not present in XRF scans, argues against the influence of WC rock crushers and instead suggests that this may be the result of a complex interference (Lomax-Vogt, et al., 2021). For these trace elements — B, As, Mo, Ag, W, Bi — we do not advise this method currently.

The primary disadvantage of this method is that, to obtain reproducible results with acceptable analytical uncertainties, each sample must be analyzed for longer than is

needed in a comparable solution-source protocol, an increase to 14 minutes for 7 replicates instead of 4 minutes for 3. Although the sample preparation time for pelletized samples is much lower (15 minutes/powder instead of 4-48 hours/glass), instrument time is more expensive than sample preparation time and this trade-off may not be economical in different labs. However, the cost of materials per sample for a pellet (~\$0.02) is substantially lower than for a glass bead (>\$10.00) when accounting for the labor, flux, acid, and consumables, so the overall cost-benefit comparison of the methods may differ between labs.

Conclusions

Although previous work on laser ablation of powder pellets has been performed, the focus on homogeneous, nano-particulate powders has meant the method was prohibitively labor-intensive and time-consuming for general-use whole-rock analysis. This work presents an alternative analytical protocol, allowing for larger particle sizes (<100 μm) and accounting for heterogeneity through increased lasing surface area. The majority of the analytes tested by this method can be measured precisely, with standard errors below 10% rel., and accurately, to within 10% of accepted values. These elements include Li, Be, Na, Mg, Al, Si, Ca, Sc, Ti, V, Mn, Co, Ga, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, and U. An analyte that should be measured with caution is B, which has a high detection limit on the instrument used, but could be accurate on a different ICP-MS. Elements that were not suitably measured by this LA-ICP-MS method include As, Mo, Ag, W, and Bi. This method will be a reliable and

inexpensive way to analyze large numbers of geochemical samples over a wide range of compositions.

Data availability

The data supporting this article have been included as part of the Supplementary Information [Supplementary Table 2.4].

Acknowledgements

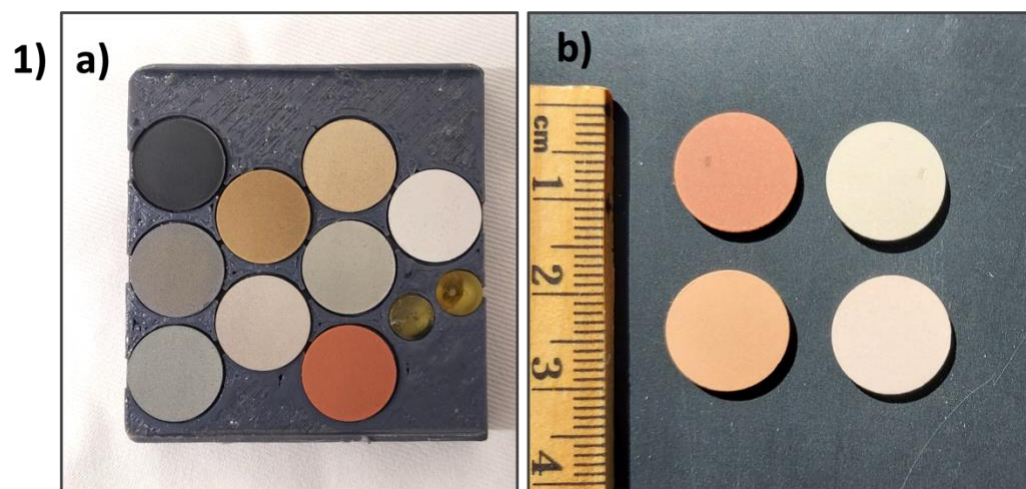
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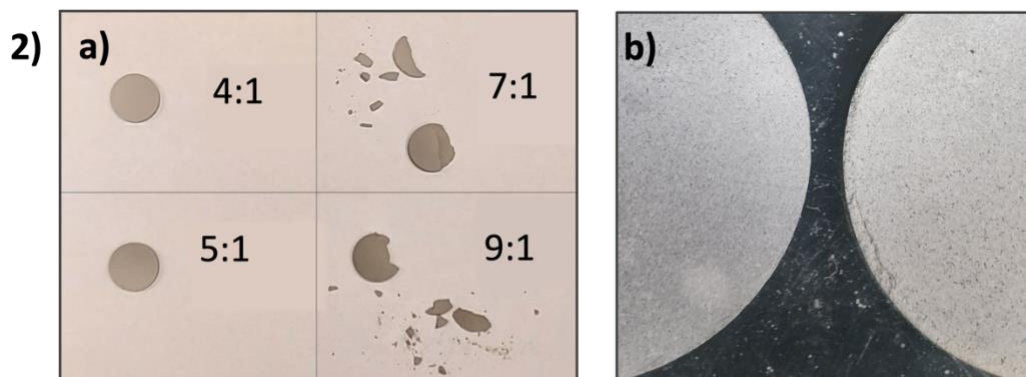
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Figures

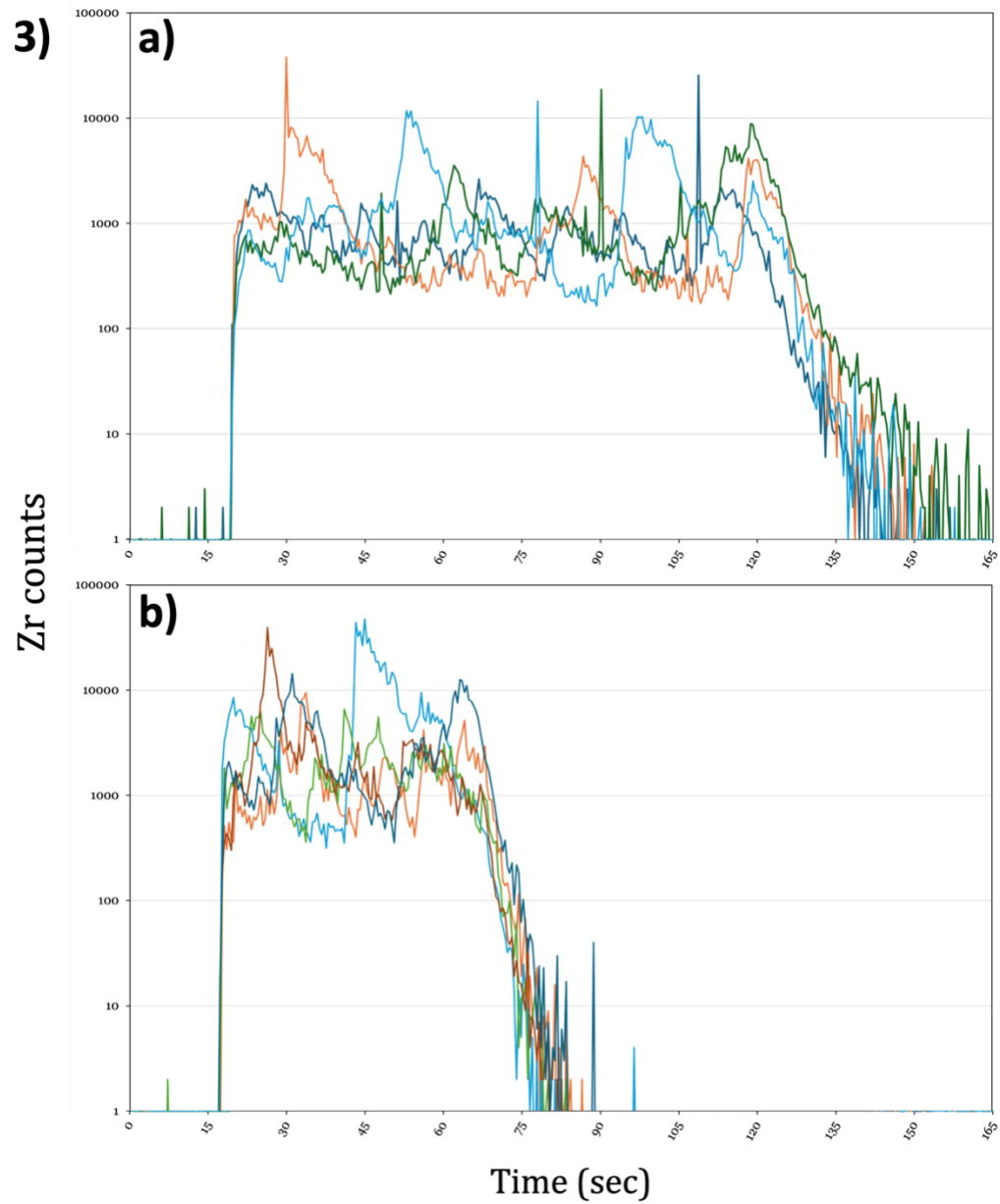
[Figure 2.1](#) – The powder pellets

a) The analysis window and ablation chamber are able to accommodate nine pellets and the glass standards, all held in a 3-D printed sample holder. b) Enlarged view of pellets with ruler for scale; pellets that have been analyzed are in the top row, with analysis lines visible as small surface heterogeneities.



[Figure 2.2](#) – Results of pellet-making conditions.

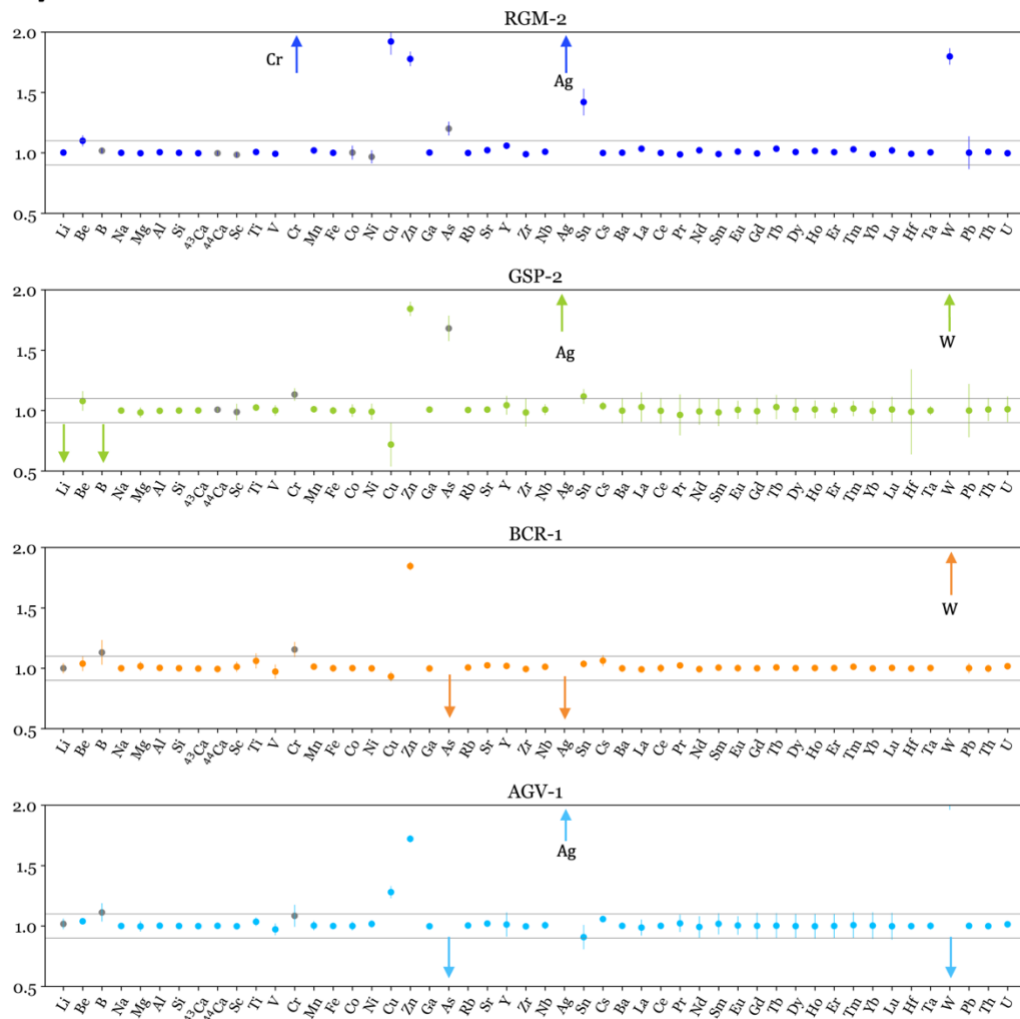
a) examples of pellets with different powder-to-binder ratios and the same total mass (400 mg) following a drop from 30 cm above the page. [b\)](#) A view through a microscope of a pellet pressed under vacuum (L) and a pellet pressed without vacuum (R). Note the damage around the edges of the edges of the right pellet and the slightly rougher texture of the interior. All pellets are 13 mm in diameter.



[Figure 2.3](#) – Replicates of zirconium measurements.

Time series of GSP-2 for 1000 μm lines (a) and 500 μm lines (b). Note that there are some spikes in some of the analyses, but all replicates contain these irregularities and none are biased towards high or low concentrations.

4)



[Figure 2.4](#) – Elemental accuracy and precision of reference materials.

Four USGS materials: a) RGM-2, (b) GSP-2, (c) BCR-1, and (d) AGV- 1. The vertical axis shows the measurement normalized to the accepted value, from GeoReM (Jochum et al., 2005), arranged by increasing Z with the standard error of the measurement presented as a vertical line. Outlier elements are indicated by arrows to allow all plots to be shown on the same scale. For each sample, elements with

known concentrations lower than the limit of detection are grey. These measurements are calibrated on BHVO-2 and STM-1. Additional reference materials examined are presented analogously in the Supplement.

Appendix II

Analytes and Materials Used

Supplementary Table 2.1a – Analytes

Analytes	Notes about elemental analyses	Calculated LoQ for LA-ICP-MS (µg/g)	Range in powders ² (µg/g)	Range in glasses ^{2,3} (µg/g)
⁷Li	High background on the specific instrument used	65.51	1.7 - 58	0.895 - 468
⁹Be	Ionization efficiency is moderate (50-80%) ¹	0.10	0.2 - 9.6	0.028 - 476
¹¹B	Ionization efficiency is moderate (50-80%) ¹ ; high background on the specific instrument used	36.14	2 - 13	0.94 - 13788
<i>F</i>	<i>Only by XRF; ionization efficiency is impractical (<0.1%)¹</i>	n.a.	70 - 3260	6.2 - 304
²³Na		2049.51	740 - 66,600	0 - 102,000
²⁴Mg	Concentration range of NIST glasses not suitable for samples	16.11	600 - 298,000	34 - 53,200
²⁷Al		54.23	2400 - 123,400	10,000 - 98,000
²⁸Si ²⁹Si	²⁸ Si measured as ISTD	10409.68 (²⁹ Si)	184,000 - 344,000	265k - 339,000
³¹P	<i>Ionization efficiency is impractical (33%)¹, analyses on ICP-MS are not quantitative</i>	n.a.	20 - 11,300	0 - 413

S	<i>Only by XRF; ionization efficiency is impractical (<1%)¹</i>	n.a.	19 - 650	291 - 575
Cl	<i>Only by XRF; ionization efficiency is impractical (14 %) ¹</i>	n.a.	10.7 - 500	102 - 274
³⁹K	<i>Strongly preferred by XRF due to mass spread ⁴⁰Ar interferences</i>	n.a.	40 - 44,700	29 - 6,570
⁴⁴Ca ⁴³Ca	Dominant mass (40) overlaps with ⁴⁰ Ar; ⁴⁴ Ca overlaps with CO ₂	32135.59 (⁴⁴ Ca) 5102.40 (⁴³ Ca)	900 - 345,000	45,000 - 85,000
⁴⁵Sc		11.25	0.7 - 77.6	0.026 - 455
⁴⁷Ti		4.24	60 - 16,400	2.65 - 4718
⁵¹V		1.32	8.7 - 410	0.228 - 3573.86
⁵²Cr	⁴⁰ Ar ¹² C ⁺ overlap	24.97	4 - 15500	0.4 - 5110.99
⁵⁵Mn		24.47	273 - 1700	0.609 - 4933.29
⁵⁶Fe	⁴⁰ Ar ¹⁶ O ⁺ overlap	328.86	13,000 - 93,800	16 - 5783
⁵⁹Co		5.39	0.9 - 120	0.051 - 5772.79
⁶⁰Ni	Potential complications from cone	4.92	3 - 3780	0.435 - 5736.67
⁶³Cu	Potential complications from cone	0.77	2.85 - 129.3	0.7 - 5592.06

⁶⁶Zn	Ionization efficiency is moderate (50-80%) ¹	0.91	33 - 235	1.33 - 6322.73
⁷¹Ga		0.91	0.94 - 35	0.5 - 433
⁷⁵As	Ionization efficiency is moderate (50-80%) ¹	13.93	0.22 - 4.6	0.2 - 325
⁸⁵Rb		3.98	2 - 245	0 - 4517.20
⁸⁸Sr		0.36	0.53 - 700	41.72 - 6443.43
⁸⁹Y		0.06	0.03 - 42.5	0.0288 - 6701.11
⁹⁰Zr		0.18	0.13 - 1210	0.0951 - 5841.04
⁹³Nb		0.03	0.03 - 270	0.0194 - 465
¹⁰⁷Ag	Imprecision in reported concentrations ² ; 109 also examined	0.10	<0.089	0.048 - 251
¹¹⁸Sn	Potential complications from brass mounts	1.21	0.48 - 6.8	1.18 - 430
¹³³Cs		0.46	0.002 - 10	0.027 - 6696.90
¹³⁷Ba		0.75	16 - 1340	2.31 - 6950.32
¹³⁹La		0.04	0.013 - 180	0.0298 - 6676.48
¹⁴⁰Ce		0.004	0.02 - 410	0.0292 - 6488.65
¹⁴¹Pr		0.003	0.003 - 51	0.015 - 448
¹⁴⁶Nd		0.04	0.0121 - 200	0.0227 - 430

¹⁴⁷Sm		0.07	0.003 - 27	0.0164 - 453
¹⁵³Eu		0.35	0.0008 - 3.35	0.0146 - 447
¹⁵⁷Gd		2.08	0.003 - 12	0.0162 - 449
¹⁵⁹Tb		0.003	0.0006 - 1.39	0.0145 - 437
¹⁶³Dy		0.03	0.004 - 7.75	0.0173 - 437
¹⁶⁵Ho		0.01	0.001 - 1.5	0.0169 - 449
¹⁶⁶Er		0.01	0.0046 - 4.19	0.0157 - 455
¹⁶⁹Tm		0.01	0.0009 - 0.69	0.0144 - 435
¹⁷²Yb		0.07	0.0075 - 4.13	0.0171 - 450
¹⁷⁵Lu		0.03	0.0016 - 0.6	0.0145 - 439
¹⁷⁸Hf		0.05	0.005 - 28	0.0154 - 6308.96
¹⁸¹Ta		0.02	0.001 - 17.9	0.0299 - 446
¹⁸²W	Possible contamination during sample prep; 183 and 184 also examined	0.08	0.012 - 3.6	0.043 - 444
²⁰⁶Pb ²⁰⁷Pb ²⁰⁸Pb	Potential complications from brass mounts	0.16 (²⁰⁶ Pb) 0.18 (²⁰⁶ Pb) 0.08 (²⁰⁶ Pb)	1.46 - 42	1.85 - 6999.52
²³²Th		0.01	0.004 - 105	0.0252 - 7364.42

^{238}U		0.01	0.002 - 8.46	0.0721 - 6646.50

¹Houk 1978; ² GEOREM (note that differences in precision are due to different methods), ³ Corning 2002

Supplementary Table 2.1b – Materials

Source	Name	Rock Type
USGS	AGV-1	Andesite
USGS	AGV-2	Andesite
USGS	BCR-1	Basalt
USGS	BCR-2	Basalt
USGS	BHVO-2	Basalt
USGS	GSP-1	Granodiorite
USGS	GSP-2	Granodiorite
USGS	RGM-2	Rhyolite
USGS	STM-1	Syenite
USGS	SDC-1	Schist
GSJ	JGB-2	Gabbro
GSJ	JH-1	Hornblendite
USGS	DTS-2b	Dunite
USGS	COQ-1	Carbonitite
USGS	BIR-1a	Basalt
USGS	W-2b	Diabase
USGS	MAG-1	Marine Sediment
USGS	NKT-1	Nephelinite
USGS	NOD-A-1	Mn-nodule
USGS	NOD-P-1	Mn-nodule
USGS	QLO-1a	Qtz Latite
USGS	SCO-2	Shale
USGS	SSAR-1	River Sediment
GSJ	JG-2	Granite
USGS	G-2	Granite
USGS	DNC-1	Diabase
USGS	W-2a	Diabase

Agilent 8800 Run Parameters

The instrument was tuned on a stock tuning solution in no-gas, single-quad solution mode. Tuning included electron-multiplier calibration; signal optimization on ^7Li , ^{89}Y , and ^{205}Tl ; oxide and doubly-charged ion measurements for $^{140}\text{Ce}^+$, $^{70}\text{Ce}^{+2}$, and $^{140}\text{Ce}^{16}\text{O}^+$; and pulse/analog detection factor calculation for every analyte.

Supplementary Table 2.2 – Typical equipment parameters

RF power	1500 W	Nebulizer gas flow	1.15 L/min
Matching	1.3-1.4 V	Option gas	95%
Sample Depth	8.1 mm	Makeup gas flow	0.2 L/min
S/C Temp	19 °C		
Extract 1	-15 V	Omega Bias	-100 V
Extract 2	-185 V	Omega Lens	0.5 V

Integration time for all analytes is 0.0050 sec

XRF Calibration

Samples were analyzed on a Pan-Analytical Zetium X-ray Fluorescence analyzer. The system calibrated 16 elements successfully (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn), including three elements (F, S, Cl) not attempted with laser ablation and two elements (P, K) not suitable for laser ablation. All elements were manually peaked, and had backgrounds and interferences determined on the calibration standard with the highest concentration, before the calibration with the USGS and GSJ reference materials described in the main text. The accelerating

potentials and currents are displayed below, and all samples were analyzed in custom stainless-steel holders with a ½” (12.7mm) diameter hole while the instrument used a 10mm collimator mask.

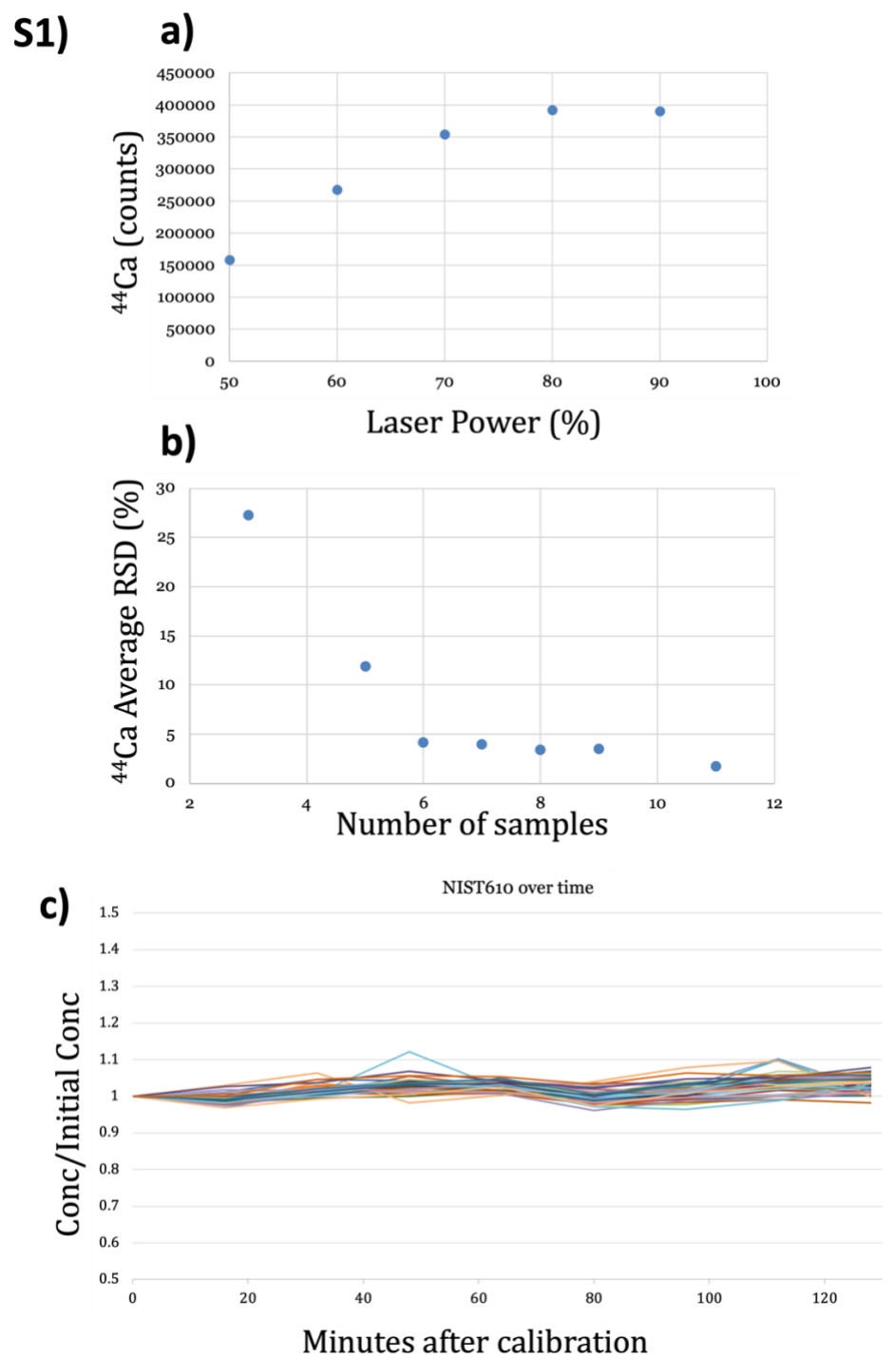
The detection limit for F by this method is fairly high (~100 µg/g), making this method impractical for rocks with low concentrations. Individuals interested in analyzing such rocks could make larger pellets (e.g., 25 or 40 mm diameter) for the explicit purpose of measuring F (and Cl or S), as the larger analytical surface would improve the samples’ counting statistics.

Supplementary Table 2.3 – XRF Analytical conditions

elements	kV	mA	Crystal	Collimator	Detector	Limit of Detection, µg/g*
F Na Mg	25	160	PX1	700 µm	Flow	113.4 244.6 227.0
Al Si	25	160	PE	300 µm	Flow	278.5 237.0
P S Cl	25	160	Ge	300 µm	Flow	23.7 8.3 27.7
K Ca Ti Cr Mn	25 30 40 50 60	160 133 100 80 66	PX10	300 µm	Flow	69.7 131.7 62.7 20.9 18.3
Fe Cu Zn	60	66	PX10	300 µm	Scint	53.3 3.3 3.9

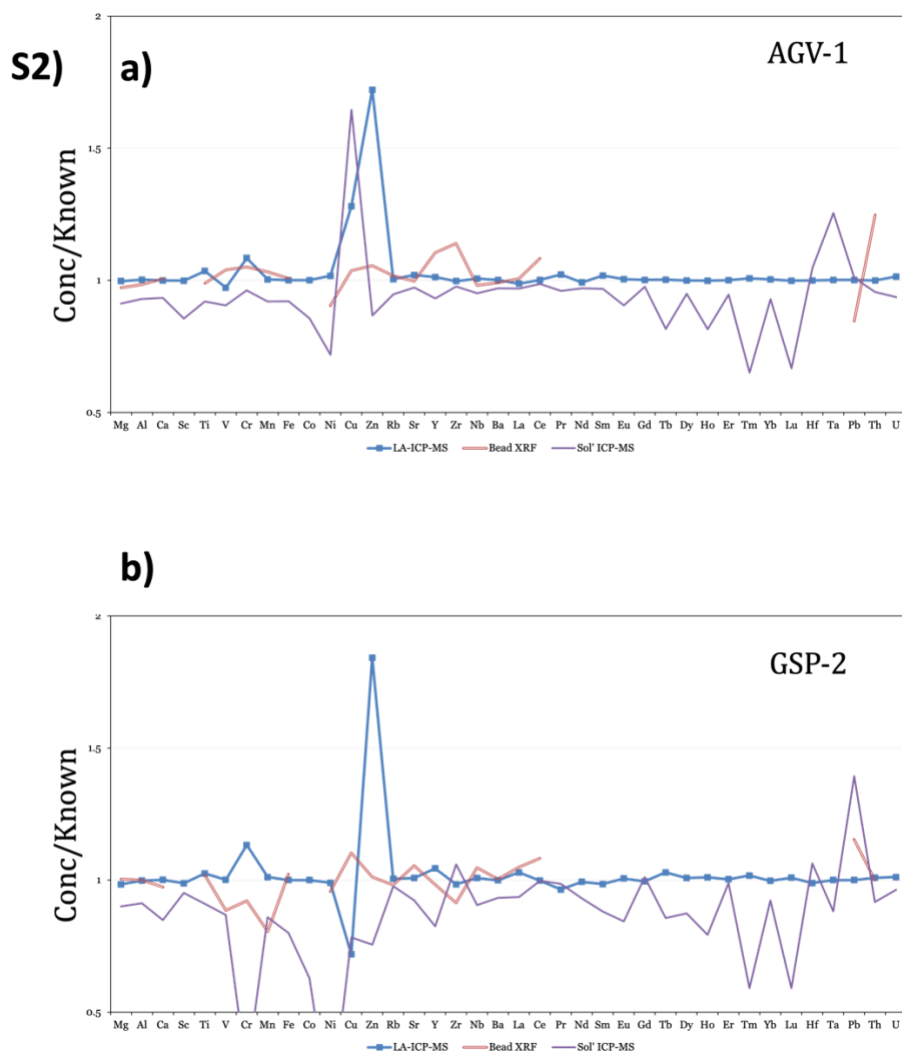
Files in deposit: Analytical data (Supplementary Table 2.4)

Supplementary Figures



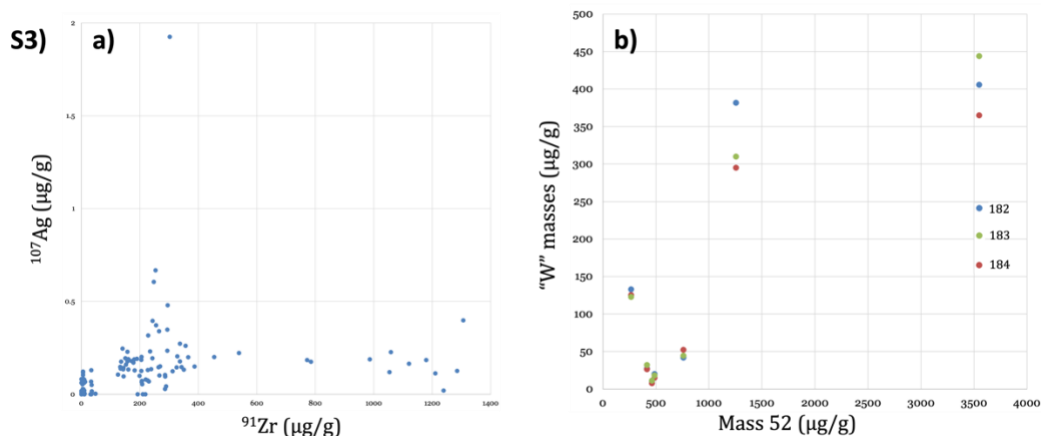
[Supp. Fig. 2.1](#) – Quantitative results of analytical conditions from AGV-1.

a) Counts of ^{44}Ca as a function of laser power. Above 80%, there is no additional signal return. b) The average relative standard deviation of ^{44}Ca versus the number of lines included in the average. To calculate this, n random lines were chosen from 12 analyses and their standard deviation was calculated, repeated over many permutations. c) Example from a ~2 hour analytical session showing there is no systematic drift (i.e., degradation of signal). The erratic line is Cu.



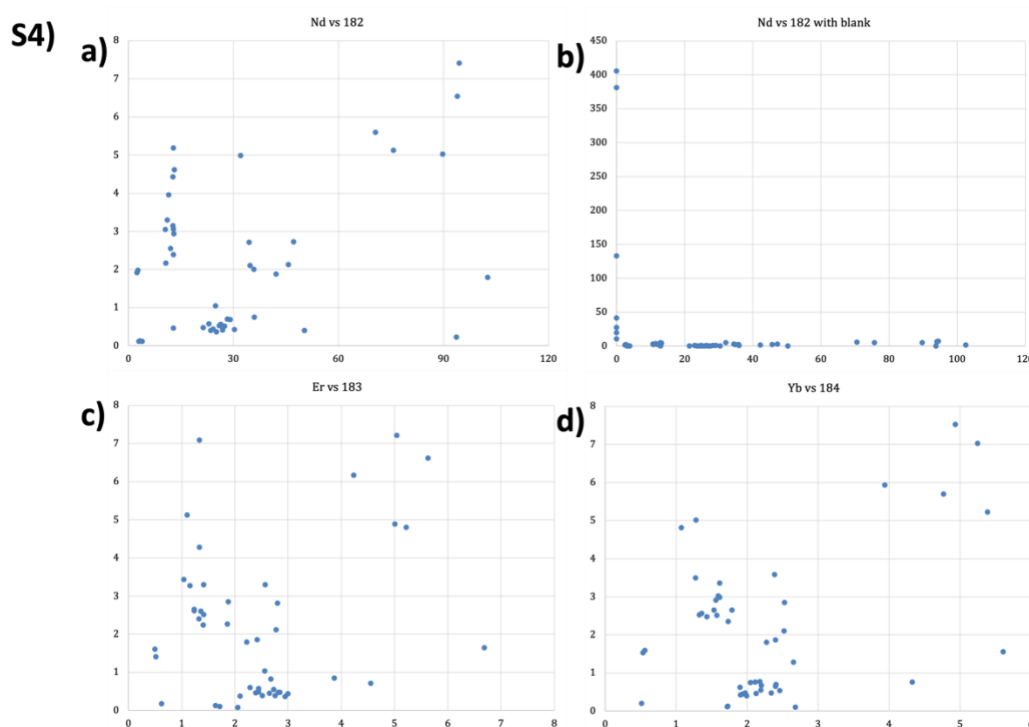
[Supp. Fig. 2.2](#) – In-house method comparison.

Comparison of in-house analytical methods for 2 reference materials, AGV-1 (a) and GSP-2 (b), normalized to known values (Jochum et al., 2005). Solid lines with points are LA-ICP-MS of pellets (this method), doublet lines are XRF analysis of lithium borate beads, thin lines are ICP-MS measurements of lithium borate beads dissolved in HF/HNO₃ acids. Zinc, one of the Elements of Note, behaves appropriately in XRF bead measurements.



[Supp. Fig. 2.3](#) – Elements of note and their possible isobaric interferences.

a) Ag (mass 107) does not correlate with ^{91}Zr in the reference materials, precluding the dependence on $^{91}\text{Zr}^{16}\text{O}$. (b) Mass 52 versus the three interrogated tungsten masses in the cellulose blank. Both W and Cr should plot close to the origin, according to XRF data and the cellulose certification, but instead they are both elevated and appear to be somewhat correlated.



[Supp. Fig. 2.4](#) – Probable mass isobaric interferences for W.

Various “W” mass isobaric interferences in analyzed reference materials in $\mu\text{g/g}$: a) Nd versus mass 182 (argide ion), b) same as a) but including cellulose blank, c) Er versus mass 183 (oxide ion), d) Yb versus mass 184 (carbide ion). There is very little correlation between the polyatomic ions and the tungsten masses, and this hypothesis fails dramatically when considering the cellulose blank.



Supp. Fig. 2.5 – Additional reference materials

Elemental accuracy and precision of three additional USGS reference materials without preferred values: (a) MAG-1, (b) Nkt-1, (c) QLO-1a. The vertical axis shows the measurement normalized to previously published values, from GeoReM, arranged by increasing Z with the standard error of the measurement presented as a vertical line [Supplementary Table 2.1]. For each sample, elements with known concentrations lower than the limit of detection are grey. These measurements are calibrated on BHVO-2 and STM-1.

CHAPTER III

HALOGENS IN GRANITOIDS: A GLOBAL REVIEW

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Abstract

This study presents a global survey of the whole-rock fluorine content (F) of silica-rich granitoids from around the world. Due to complications in measuring fluorine, few publications about the geochemistry of granitoids report bulk concentrations of fluorine and other halogens. After surveying the literature, we compiled ~280 sources across 78 countries and territories that report whole-rock F of granitoids, which results in data for more than 4000 localities and 800 unique plutons. This data is analyzed for correlation of whole-rock major and trace element concentrations, as well as mineralogy and inferred tectonic setting, with F. As expected, F content in granitoids behaves most similarly to other fluid-mobile, incompatible elements like Rb, with weaker correlations to the content of some high field-strength elements (HFSE). Analysis has also involved grouping by Fe-number, modified alkali-lime index*, and alumina saturation index*, and granitic type. Additional observations include the highest F in A-type granites, as well as in peraluminous granites of all types. Of the authors that include mineralogical observations, most report fluorinated accessory phases like Ap, Flr, Trm, and Tpz, as well as potential hosts like zinnwaldite (an F-bearing mica), and amphiboles. Peralkaline magmas show a stronger positive HFSE-F relationship than peraluminous magmas, corroborating the experimental observation that alumina content has a significant effect on a melt's ability to complex and mobilize immobile elements like Zr and Nb.

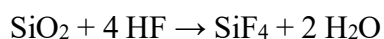
Introduction

Fluorinated granites are the subject of studies around the world. Interest is due, in part, to their affiliation with magmatic and hydrothermal ore deposits, like the Bohemian Massif in Germany (e.g., Forster et al., 1999) or the Dahutang district in China (e.g., Yang et al., 2022), that often hosting economically viable concentrations of metals such as Nb, Ta, and rare-earth elements (REEs; the lanthanides $\pm$ Y, Sc). In particular, A-type (Bonin, 2007) and/or ferroan (Frost et al., 2001) granites are recognized for having high concentrations of fluorine, up to several orders of magnitude above “typical” crustal concentrations (Wedepohl, 1995). In some cases, the most fluorinated samples of a locality are marginal altered rocks, like greisens, or pegmatitic veins (e.g., “NYF type” pegmatites), although there are examples of plutons with extremely enriched F concentrations across the whole body (e.g., ongonite). The term *granite* in this work will be used exclusively *sensu lato*, defined as an igneous, intrusive body of felsic nature, not the subset of these rocks with a limited modal range of quartz, plagioclase, and alkali feldspar. Additionally, the groupings of granite by type or chemical characteristic will be defined explicitly in the text.

Unlike the other halogens (Cl, Br, I), fluorine preferentially partitions into melts over fluids, although it can easily be remobilized out of minerals by hydrothermal fluids (Manning, 1981; Webster & Holloway, 1990; Dolejš and Zajacz, 2018 and references therein). Its ionic radius is comparable to both O^{2-} and the hydroxyl ion (Li et al., 2017), which allows compatibility in many hydrated phases. The most important of

these include minerals in the mica and amphibole families, where F^- substitutes easily for OH^- (e.g., fluorannite, $KFe^{2+}_3Si_3AlO_{10}F_2$). Other common hosts of fluorine include the eponymous fluorite (CaF_2), fluorapatite [$Ca_5(PO_4)_3F$], topaz ($Al_2SiO_4F_2$), and cryolite (Na_3AlF_6). The vast majority of commercial fluorine comes from mining fluorite, and F is used in a wide variety of industrial settings, from steel and ceramic production to polymer synthesis (e.g., Chamber and Holliday, 1975).

The exact mechanism by which fluorine affects metals in fluids and melts is unknown, but there is some consensus in the field. Many publications have observed that in the case of high field strength elements (HFSEs; Zr, Hf, Nb, Ta), the solubility and mobility of elements in melts is not due to the production of F-HFSE species, but rather the depolymerization of the silica melt (London, 1987; Keppler, 1993; Aseri et al., 2015; etc.). This is closely related to the ability of HF to dissolve glass through the formation of fluorinated silicon species (Chambers and Holliday, 1975; Spierings, 1993):



The presence of magmatic F strongly depresses the granite liquidus temperature, melt viscosity, and quartz fractionation (Manning, 1981; Dingwell et al., 1985; Dingwell and Mysen, 1985; Weidner and Martin, 1987; Giordano et al., 2004; Pichavant, 2022), potentially enabling extreme enrichment of metals in melts. Furthermore, work by Liu et al. (2024) and others demonstrate that nominally fluid-immobile

elements like Nb become highly mobile in fluorinated fluids across a range of temperatures and pressures.

However, despite the importance of F content to the evolution of silicic magmas, it remains a challenging element to measure and is often omitted from routine geochemical investigations. To measure F in whole-rock samples, ion-specific electrode (ISE; also written ion-selective or specific-ion electrode) measurements were popular in the 20th century (Ingram, 1970). However, this method is less common in recent petrologic publications, as such analyses are not the most economically efficient (i.e., only one element can be analyzed at a time with this approach) and it is now performed primarily by commercial laboratories. On the other hand, wavelength-dispersive X-ray fluorescence (XRF) is a method capable of measuring many elements at once, but many instruments struggle to detect F as a trace element due to diffraction crystal limits and the weak characteristic X-rays of F (Hasany et al., 1991; Tarsoly et al., 2010). Without high-resolution analyses, the overlap of the F K-alpha emission line with the L-alpha lines of Mn and Fe can cause spectral interferences, and the high temperature fusions typical for sample preparation may induce volatilization and F loss (e.g., Feng et al., 2011). Wet chemistry methods are fairly common in research papers in the late 20th century, but have declined in popularity like ISE due to the time-intensive and expensive nature of the method. Instrumental neutron activation analysis (INAA) is another potential method, although F, as a light element, is not the most readily activated and there has

been a global decline of INAA facilities over the last few decades (e.g., Nakamoto et al., 2007). Other less frequent methods include proton-induced gamma-ray emission spectrometry (PIGE; Roelandts et al., 1987), colorimetry (e.g., Woolley & Jones, 1987), and pyrohydrolysis ion chromatography (e.g., Kohler et al., 2009). In contrast to whole-rock measurements, in situ methods, including electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS), are widely available for mineralogical analyses (Hanley and Koga, 2018).

A previous compilation of fluorine in granitic rocks was conducted by Bailey (1977), using a detail-oriented approach to a small number of studies. More recent reviews (Harlov and Aranovich, 2018) and Fuge (2019) examine crustal rocks and reservoirs more broadly, and are limited to a few samples or publications per rock type (i.e., 1 or 2 references for average global granite). Such limited and uneven coverage makes it difficult to evaluate which patterns are general and which are specific to particular compositional lineages or post-magmatic histories. Further, many claims about F-enrichment implicitly rely on mixed and sometimes subjective classification language (e.g. I-S-A-type terminology, descriptive labels such as “rare-metal granite,” or field-based rock names without consistent chemical context).

This contribution presents compiled data from 280 sources, representing 78 countries and territories around the world, and whole-rock geochemistry analyses for over 4000 samples. We evaluate how F covaries with major- and trace-element chemistry, reported mineralogy, and inferred tectonic setting, and we place samples in a

consistent geochemical framework using calculated indices. A central outcome is that high fluorine occurs across multiple granitoid lineages, but at elevated F the covariation between F and HFSE differs systematically with bulk composition. This implies that fluorine content alone is not predictive of HFSE enrichment; instead, the effect of fluorine on “rare-metal” behavior depends on major-element context (e.g., aluminosity/alkalinity), consistent with experimental evidence that melt composition influences HFSE solubility and mobility.

Methods

Compilation Methods

In order to collect an unbiased collection of samples from granites globally, publications were identified and curated manually, rather than using precompiled data from an online database. There are several reasons for this approach: to preserve the authors’ field and petrologic descriptions (e.g., mineralogy, alteration, textures) of the samples, contextual interpretations (i.e., tectonic setting), and to understand the methods and assumptions made during analysis (e.g., was Fe_2O_3 measured directly, calculated from equivalent FeO , or estimated from an assumed $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio). Several lists of sources were taken from previous compilations (e.g., Dolejš and Baker, 2004), but all data was manually curated.

Publications were identified using multiple search engines and keywords strategies. Searches included F-specific methodologies, F-bearing minerals, and general terms like “halogen”. However, the majority of the searches intentionally omitted these

terms to avoid preferentially capturing studies of high-F concentration systems. Searches were performed in multiple languages to include regional and international publications, including those published in non-English journals. To supplement online searches, physical journals with no digital equivalent were also searched in the California Institute of Technology Division of Geological and Planetary Sciences library. In some cases, complementary data for the same sample suites were distributed across multiple publications, so there are sources that have been added to this compilation that contain no whole-rock F data, but contain complementary geochemistry or petrographic descriptions (e.g., the Nigeria Younger Granites analyzed for Li in Bowdon, 1965, and for other elements in Butler et al., 1961),.

Inclusion criteria and dataset fields

The minimum requirements to be included in compilation were: (1) F measured in the whole-rock, (2) a description of the rocks indicating at least one sample from a suite is granitic, and (3) at least five additional whole-rock geochemical measurements. In addition to whole-rock chemistry, information about the geologic setting (e.g., orogeny and tectonic province association, if any), alteration, mineralization, F analytical method, and modal mineralogy were compiled. In some cases, fields are not applicable (i.e., “Craton” for a sample not collected from a craton). In others, the information is not reported (i.e., alteration style). Where possible, samples are reported with the name or order number reported in the original text. In many cases, sample location coordinates are not provided in the text, so these

numbers were estimated from published maps. Some details (e.g., modal abundances) are reported as averages for a lithologic group and are therefore the same value for all relevant samples. When reported in the sources, whole-rock isotope data, as well as whether mineral chemistry is available, are included.

Geochemical parameters

Whole-rock geochemical parameters, like the aluminum saturation index (ASI), as well as normalization values (e.g., $[\text{La/Yb}]_n$ where n may indicate chondrite, primitive mantle, etc.) are not calculated consistently across studies. To avoid ambiguity, all geochemical parameters used in this work are defined explicitly and are recalculated from reported whole-rock compositions, rather than relying on reported values. Additionally, to accommodate the differences in mineralogical methodology and nomenclature, discussions of mineralogy are restricted to subsets of the compilation with similar approaches. The reason for this is that a publication limited to optical microscopy would not necessarily be able to identify oxides and opaque minerals with the same detail and precision as a study that used Raman, SEM, or EPMA techniques. The former can be identified in the compilation by “X” markers in the oxide mineral columns, while the latter will have the specific phase identified.

The following conventions will be followed in the discussion below:

- Fe* - Fe number (unitless), the relative proportion of Fe to Mg, calculated as $\text{FeO}^T/(\text{FeO}^T+\text{MgO})$ using weight percent oxides with all iron as FeO (Miyashiro, 1970).
- ASI - Aluminum saturation index, or the amount of aluminum relative to the amount in feldspar, calculated on a *molar* basis as $[\text{Al}]/(2*([\text{Ca}]-1.67[\text{P}])+[\text{Na}]+[\text{K}])$ to accommodate apatite (Zen, 1988; Frost et al., 2001). This number is similar to but not to be confused with A/NK and A/CNK (which are ratios calculated on a *molar oxide* basis)
- MALI* - Modified alkali-lime index, or the relative proportion of alkalis to calcium for a given silica content, calculated as $[(\text{Na}_2\text{O}+\text{K}_2\text{O}-\text{CaO}) + 44.72 - (1.094*\text{SiO}_2) + (0.00527*\text{SiO}_2^2)]$ using weight percent oxides, corresponding to deviation from the alkali-calcic and calcic-alkali boundary of Frost et al. (2001). Positive numbers indicate alkali-calcic to alkalic compositions and negative numbers indicate calcic-alkalic to calcic compositions.
- Modal % - Reported modal fraction are usually assumed to be volumes fraction (extrapolated from area fractions) and not mass fraction.
- LOI - Loss on ignition. The mass lost when firing a sample in an oven, generally between 900 and 1100°C. This number may be negative in the event of a highly ferrous sample that oxidizes during firing and gains more weight in oxygen than it loses in volatiles.

- Total - Sum of major oxides, as presented by the authors. Note that in the source texts, some authors include corrections for the presence of F and/or include trace elements in this sum.

After compilation, statistics (e.g., mean, median, 1st quartile, etc.) were run using a combination of custom scripts in python and Excel. When describing trace element concentrations, the medians are generally preferred to the mean because many distributions are non-Gaussian and include extreme outliers, particularly in mineralized rocks. Important reference values for F contents of major terrestrial reservoirs are presented in Table 3.1 (Hanley & Koga, 2018).

Table 3.1 – Major Earth Reservoirs of F

Reservoir or lithology	Ave. F content (µg/g)	Source
Seawater	1.3	Li, 1991
Mantle	26 (primitive mantle) 16 (mantle)	McDonough & Sun, 1995 Jagoutz et al., 1979
Oceanic crust	267 (MORB) 210-250 (MORB) 130 (primitive MORB) 400 (AOC)	Johnson, 1993 McDonough & Sun, 1995 Shaw et al., 2010 van den Bleeken & Koga, 2015
Continental crust	611 (upper cont. crust) 429 (lower cont. crust) 525 (cont. crust) 553 (cont. crust)	Wedepohl, 1995 Wedepohl, 1995 Wedepohl, 1995 Gao et al. 1998
“Average” Granite	800 (granite) 613 (granite) 5500 (SiO ₂ -oversaturated)	Bailey, 1977 Gao et al., 1998 Jambon and Zimmermann, 1990

Results: Compilation overview

The data is compiled in Supplementary Table 3.1 and all data citations for the previously published data included in the compilation are listed in SI Appendix. The results will be summarized by column in the table.

Country/Territory Sources were identified for 78 different countries and territories ([Fig. 3.1](#); STable 1). Although certain areas are underrepresented, there are no regions that are overrepresented or omitted. Australia, Canada, China, US, Russia, and Brazil are the localities with the most data points, as would be expected by land area. Finland, Germany, Nigeria, Egypt, India, Japan, Saudi Arabia, and South Africa are also highly represented, as countries with well-known and/or abundant granite intrusions (e.g., Jagoutz & Klein, 2018). Territories with distinct geologic histories from their governing country (e.g., Greenland vis-à-vis Denmark) are listed separately.

Pluton 825 different plutons are included in this compilation. Some plutons, particularly areas with ore deposits (e.g., Erzgebirge, Germany; Förster et al., 1999; Förster et al., 2009; Förster & Rhede, 2006; Webster et al., 2004) are presented in multiple publications, but all analyses included here are unique. Many studies report averages of a large number of samples, and these are denoted in the compilation by a non-zero number in the “Average” column (e.g., the reported average of 40 samples would show “40” under “Average”). Not all papers are consistent in how a pluton is defined. In some publications, different episodes of intrusion in the same area would

be given different names, while in others, the igneous body would be given one name with multiple phases. No attempt was made to standardize this in the compilation.

Age Ages are reported in Ma. Dated samples in this compilation range from 2.1 Ma to 3100 Ma ([Fig. 3.2](#)). There are peaks in sample representation during the Cretaceous (555 samples) and the Mesoproterozoic, coinciding with episodes of significant magmatism (Cretaceous superplume and the Mackenzie event, respectively; e.g., Arndt and Davaille, 2013). All major periods of Earth's post-Hadean history are represented.

Tectonic setting In some cases, there are well-established orogenic events (e.g., Pan-African orogeny), but this is not true of all study areas, and not all authors attempt to interpret the tectonic regime during which the granite intruded. The column titled "Tectonic setting" shows a standardized set of descriptors like "collisional," while the column "Detailed tectonic setting" includes the specific phrases used by the original authors (e.g., collisional, arc, continental collision, synorogenic). 1390 samples are described as collisional, 762 samples are considered late- to post-orogenic, 669 are extensional, 566 are anorogenic, 169 are intraplate (encratonic), 30 are transform (transpressional). 79 samples represent unusual tectonic environments, including large igneous provinces (LIPs) and ophiolites. These terms are inherently imperfect. For example, "extensional" environments may occur at continental rifts, at mid-ocean ridges (MORs), or in the back-arc basins of collisional arcs. Similarly, the difference between a synorogenic, collisional environment and a late-orogenic

environment is subjective and poorly defined. Therefore, these terms should be recognized as loose groupings, dependent on the interpretations and definitions of the original authors.

Lithology Not every sample included in this compilation is a granite, but the vast majority are. Many publications include granites along with affiliated rocks in an area, ranging from felsic pegmatites and aplites to more mafic granodiorites and gabbros. Less common rock types, such as trondjemites or ongonites, are also specified. In some cases, the rocks are noted as being metamorphosed, in which case, the lithology must reflect the appropriate grade (e.g., granite gneiss). The authors' primary nomenclature for samples from each study is provided in the "Lithology" column, with additional notes in the "Additional details" column. For example, a rock described as a "quartz diorite" would be listed in the former as a diorite, then as a quartz diorite in the latter. These are the names and descriptions given by the authors, not an assessment of this work. Broad information on intrusive phase or grouping, as well as select textural features, are presented in the "Additional details" column. In these cases, the initials presented are as defined in the source text.

In total, 3978 of the 4299 samples are granitoids, of which 138 are leucogranite, 27 are ongonite, 103 samples are monzonite-monzogranite, 240 are syenite-syenogranite, 259 are granodiorite-diorite, 44 are aplite, 33 are granitic pegmatite, 64 are tonalite-trondjemite, and the remaining 3070 are simply named as granites. 165 are true metamorphic rocks (gneisses and migmatites), and 49 are metasomatic in

nature (greisens and porphyrys). The remaining ~100 samples include igneous xenoliths, specialized rock types (e.g., charnockite), and more mafic affiliates (e.g., gabbro).

Type Since the introduction of the type terminology, beginning with “I” and “S” (Chappell & White, 1974; 1992) followed by “A” (Loiselle & Wones, 1979) and later, the less popular “C” (Kilpatrick & Ellis, 1992) and “M” (White, 1979) types, the granite community has been at odds with itself in the definition and usage of these terms (e.g., Barbarin 1990; Barbarin 1999). The types presented here are as reported by the original authors. It is not clear in all publications how the determination of type was made on a case-by-case basis, as definitions range beyond the original interpretation of source material. These may include, but not be limited to, geochemical indicators (e.g., Ga/Al ratios, Whalen et al., 1987), mineralogy, and tectonic environment. Of the samples with an assigned type, 1666 are A-type, 491 are I-type, 579 are S-type, and 72 are hybridized types, including 1 C/A-type, 60 A/I-types, and 11 I/S-types. There are no samples interpreted to have M-type or a transitional A/S-type character. As with tectonic setting, no attempt was made to re-interpret the authors’ original conclusions.

Alteration As a fluid-mobile element, understanding the role of post-magmatic, hydrothermal, and meteoric fluids is an important consideration when studying fluorine. To address this, information on the alteration of samples was included when possible, including terminology referencing mineral growth (e.g., sericitization) or

mineral chemistry changes (e.g., albitization). Unfortunately, not all authors include such descriptions, and many of the phrases are subjective (e.g., “less altered”) or not specific (e.g., “altered”).

F analytical method As described above, measurements of F are complicated and there are a variety of methods used across the publications. The most common method used is ISE (ion specific electrode), used for 1756 samples. XRF is the next most common method (797 samples), employing a combination of pressed pellet and fused bead sample preparations, although authors rarely report which preparation they use for F. Wet chemistry methods are fairly common too, making up 307 analyses, followed by (pyrohydrolysis)-ion chromatography (47), colorimetry (44), and high-pressure liquid chromatography (28). Rare methods include photometry (8) and spectral analysis (7).

A disappointing observation from this compilation is that a large number of papers do not state their analytical methods (776 samples) or use vague language (e.g., "chemical, spectrometric, and x-ray methods") that does not actually demonstrate their method (162). There are even some papers that explicitly list the method used for every major and trace element *except* F. Furthermore, many papers claim the use of inductive-coupled plasma methods (ICP-AES, ICP-OES, ICP-ES, ICP-S; 140 samples) or atomic absorption spectroscopy (31), but these methods cannot measure F directly, so it is unclear how these authors actually determined the concentration of fluorine.

Additional columns There are additional descriptors provided by the original authors, referencing the spatial and/or temporal context of the plutons. This includes the local block or magmatic province, shield, craton, mountain belt, and associated orogeny. Not all descriptors apply to all samples, but they are included when appropriate.

The “Paper Notes” column contains information about the paper itself, including if the modern country or territory was referred to by another name at the time of publication (e.g., “USSR in text” for papers published before 1991). If the paper is written in a language other than English, this is also where the language is noted. Inconsistent sample numbers are indicated here, as well as additional references for papers that split geochemical data into multiple publications.

Results: Fluorine Correlations

Below, correlations between fluorine and major and trace elements in the compiled dataset are presented sequentially. We focus on the relationship between F and other elements rather than treating all aspects of the dataset.

Major Elements

Consistent with Bailey (1977), there is no correlation of F with SiO₂, nor with Al₂O₃, Na₂O, or K₂O ([Fig. 3.3a](#)). There are sharp decreases in the average TiO₂ and MgO content with increasing F (Fig. 3.3b). Several elements show weak monotonic trends over most of the dataset that reverse in the most extreme F contents (>2 wt. % F). For example, average Fe₂O₃^T and CaO decrease slightly with increasing F, while average

P₂O₅ and MnO increase slightly, but above 2 wt. % F, these trends reverse (Fig. 3.3c).

In their review of granite terminology and classification, Frost et al. (2001) recommended three geochemical parameters for grouping granites based on their major element chemistry: ASI, Fe*, and MALI ([Fig. 3.4](#)). Here, we discuss the relationship of these with whole-rock fluorine.

ASI There is no systematic change in ASI with increasing whole-rock F, as both peralkaline and peraluminous melts display the same range of fluorine. However, at high fluorine (>5500 µg/g), there is an interesting deviation in the behavior of HFSEs between peralkaline and peraluminous melts. With increasing F content, Nb, Zr, and Hf reach a plateau in peraluminous melts level off at near-crustal concentrations (McDonough and Sun, 1995), but continue to increase in peralkaline magmas (see Discussion: **HFSEs**).

Fe* There is a pronounced increase in the median Fe* with increasing whole-rock F, with slightly more magnesian behavior (Fe*=0.80) in rocks with around 500 µg/g and progressively more ferroan character (up to Fe*=0.96) in rocks with more than 10,000 µg/g.

In the discussion of Fe*, it is worthwhile to bring up the principle of Fe-F avoidance, which states that in ferromagnesian minerals, the iron content is anticorrelated with fluorine (Ramberg 1952; Mason 1992), which seemingly contradicts the positive

correlation mentioned above. The behavior is due to the distortion of sites by the substitution of F^- for OH^- , shrinking the cation site and resulting in a preference for the smaller Mg^{2+} over the larger Fe^{2+} (e.g., Finch and Tomkins, 2017). However, unless the entire rock is comprised of mica and amphibole, and all iron is present as Fe(II), there is no observed influence on the whole-rock Fe-F. Additionally, in magmatic systems with fluorite, apatite, or Fe-free micas, the F budget of a pluton may end up dominated by phases unaffected by Fe-F avoidance (Teiber et al., 2014). Further study of the mineral data present by studies in this compilation could illuminate nuances to this behavior on a global scale, but are outside the scope of this study.

MALI*As with ASI, there is no significant relationship between the calcic or alkalic character of a sample and its F content. Samples span in both the calcic/calcic-alkalic ($MALI^* < 0$) and alkalic/alkali-calcic ($MALI^* > 0$) categories across the range of whole-rock fluorine. At very low F ($< 200 \mu g/g$), $MALI^*$ values are slightly alkalic on average (0.93), decreasing in rocks with crust-like F (200-550 $\mu g/g$) to slightly calcic values (-0.15), increasing towards alkalic (0.81) in moderately enriched samples (F from 550-5,500 $\mu g/g$), and decreasing again in the extremely enriched rocks (F > 2 wt. %) to slightly calcic $MALI^*$ (-0.70).

Trace Elements

Several trace elements show strong correlations with whole-rock fluorine ([Figs. 3.5 and 3.6](#)). Results are summarized below by geochemical chemical character of the elements (e.g., White, 2005).

Alkalis & Alkaline Earths The highly fluid-mobile alkali metals Li, Rb, and Cs show more than an order of magnitude increase in median concentrations between rocks with crust-like F (200-550 $\mu\text{g/g}$) and highly enriched F (>5500 $\mu\text{g/g}$; Fig. 3.5a). Median Li, for example, increases from 31 $\mu\text{g/g}$ to 470 $\mu\text{g/g}$ across this range. These elements, like fluorine are generally concentrated in highly evolved magmas like granites, like fluorine, so this is not unexpected. However, the alkaline earth elements show less regular behavior. Be increases with increasing F, from 4.2 to 11.2 $\mu\text{g/g}$ between rocks with crust-like and enriched F contents. Sr and Ba, on the other hand, decrease from 140 to 23 $\mu\text{g/g}$ and 480 to 43 $\mu\text{g/g}$, respectively, across the same populations (Fig. 3.5b).

Transition Metals The first row transition metals also display a range of relationships with increasing F, from weakly negative (e.g., V; Fig. 3.5c) to weakly positive (e.g., Zn; Fig. 3.5d) to no observable correlation (e.g., Cr). A few other transition metals, including Cd and Au, may have slightly positive correlations with increasing F, while Ag and Hg show no relation, but these elements are infrequently measured and subject to the effects of small-number statistics. Mo shows a minimally positive correlation, increasing from 1.3 to 3.0 $\mu\text{g/g}$ between crust-like and enriched F contents. W shows a much stronger correlation over the same range of F, 3.0 to 21

μg/g respectively. Platinum group elements (PGEs) data were sparse and are not discussed further.

HFSEs The behavior of HFSEs with respect to fluorine is complicated. As mentioned above, at high F (>5500 μg/g), Zr, Nb, and Hf diverge into two populations: one with a strong enrichment correlated with F content and the other with a crust-like concentration that is invariant with respect to whole-rock F ([Fig. 3.6](#)). Of note, this is not observed in Ta, which strongly correlates with F across the entire range ([Fig. 3.6d](#)). The correlated enrichment is observed in the peralkaline samples, while the flat population is observed in peraluminous rocks. The fractionation of these geochemical twins (Zr/Hf and Nb/Ta) is often interpreted to be due to hydrothermal activity, as it is believed that magmatic processes are ineffective at separating elements with comparable ionic charge and radius (CHARAC; Bau 1996). As seen in [Fig. 3.7a](#), Zr/Hf shows CHARAC behavior across the range of fluorine content up to 5500 μg/g, with elemental ratios from 35 to 24 (CHARAC range of 26-46; Bau 1996). At higher F concentrations, the ratio decreases to 17, and the difference between high-F peraluminous and peralkaline granites is a factor of about 2.5. On the other hand, Nb/Ta is barely CHARAC at low F (9-12, with a CHARAC range of 12-22; calculated as in Bau 1996), decreasing to 2 at high F ([Fig. 3.7b](#)). Unlike Zr/Hf, the difference between peralkaline and peraluminous Nb/Ta ratios in high F samples is an order of magnitude.

Post-Transition and Metalloids Trace elements in the metalloid and post-transition metals (Groups 13 and 14), like Ga and Sn, occasionally show positive trends with fluorine content ([Fig. 3.5e](#)). There are similar patterns in Ge and Tl, but these are uncommon elements to measure, so the sample sizes are much smaller ($n = 184$ and 361 , respectively). The enrichment in median values for these elements between rocks with crust-like to high F ranges from a factor of ~ 2 (19 to 36 $\mu\text{g/g}$ in Ga) to an order of magnitude (5 to 50 $\mu\text{g/g}$ in Sn). The other members of these two groups, B and Pb, show very little enrichment across the same composition (28 to 40 $\mu\text{g/g}$ and 25 to 36 $\mu\text{g/g}$, respectively). However, there are select samples with extremely high F (>2 wt. %) that have significant B and/or Pb (over $10,000$ and 3800 $\mu\text{g/g}$, respectively; [Fig. 3.5f](#)). In Group 15, As increases by a factor of 4 between crust-like and enriched F concentrations (2 to 8 $\mu\text{g/g}$, respectively), Sb does not show any trend, and Bi increases dramatically (0.7 to 37 $\mu\text{g/g}$) across the same range ([Fig. 3.5g](#)). It should be noted that the high Bi concentration includes a population of samples from Bi-deposits, and there are a small number of analyses for Bi ($n = 297$).

Volatiles When compared with fluorine, the other halogens show no obvious trends. Cl and Br are both independent of F ([Fig. 3.5h](#)), but are slightly correlated with each other, though the generalizability of this is limited by the small number of Br measurements. There is a slight increase in the median whole-rock CO_2 with increasing F, from 1300 $\mu\text{g/g}$ in crust-like samples, to 1650 $\mu\text{g/g}$ in enriched samples,

and 2200 $\mu\text{g/g}$ in rocks with more than 2 wt. % F. There is no obvious relationship between S and F.

REEs REE contents, including individual element concentrations ([Fig. 3.8a](#)), the sum of light REEs, sum of heavy REEs, and sum of all REEs, show no correlation with F content. However, there is a depletion of light REE relative to heavy REE (evaluated as the chondrite-normalized La/Yb ratio, $[\text{La/Yb}]_{\text{CN}}$) with increasing F, decreasing from median ratios of 8.7 in rocks with crust-like F (200-550 $\mu\text{g/g}$) to 2.7 in highly F-enriched rocks ($F > 5500 \mu\text{g/g}$; Fig. 8b). Similarly, the tetrad effect ($T_1 = [(\text{Ce}*\text{Pr})^{0.5}/(\text{La}*\text{Nd})^{0.5}]_{\text{CN}}$; $T_3 = [(\text{Tb}*\text{Dy})^{0.5}/(\text{Gd}*\text{Ho})^{0.5}]_{\text{CN}}$; $T_{1,3} = [T_1 * T_3]^{0.5}$; definition by Irber, 1999) shows a slight increase in median $T_{1,3}$ from 1.0 with crust-like F to 1.2 in highly fluorinated granites.

Th and U Th and U are sometimes considered HFSE, as they have high charges, or as rare-earths, due to the prevalent role of f-orbitals in their bonding behavior. However, these two elements are not true members of either classification. Of note, U can be fluid-mobile in oxidizing environments. Th displays behavior similar to Zr and Nb, but instead of highly fluorinated peralkaline melts showing a positive correlation and peraluminous rocks being constant, Th content is invariant in highly fluorinated peralkaline granites and negatively correlated with F content in peraluminous ones ([Fig. 3.6e](#)). Median Th content increases in all granites between crust-like and enriched fluorinated systems (13 to 39 $\mu\text{g/g}$), and above 5500 $\mu\text{g/g}$ F, peralkaline rocks continue to a median Th of 53 $\mu\text{g/g}$ while peraluminous melts

decrease to 4 µg/g. U increases slightly with F content, from 3.2 µg/g in rocks with crust-like F up to 15.9 µg/g in more enriched samples (Fig. 3.6f).

Geochemical Parameters - F correlations

There are moderate correlations of Rb/Sr, Rb/Ba, K/Rb, and Eu* (defined as $[Eu/(Sm \cdot Gd)^{0.5}]_{CN}$) with F concentration, which are positive in the first two and negative in the latter two (Fig. 3.8c). This is not surprising, as these petrologic ratios are often invoked in reference to the fractionation of magmas, which preferentially partition more incompatible elements into the remaining, evolved melt. As an incompatible and fluid-mobile element, F behaves very similarly to Rb in most crystallizing phases, deviating only in some late-stage minerals like fluorite.

Other Descriptor - F correlations

Trends in Type There does appear to be a small but resolvable difference between the fluorine contents of different granite types. A-type granites, whether they are defined by Ga/Al ratios above 2.6×10^{-4} (Whalen et al., 1987), by anorogenic settings (Loiselle & Wones, 1979), or by anhydrous character (e.g., Clemens et al., 1986), generally have higher whole-rock fluorine than other types. There is a shift in the median, from 1600 µg/g in A-type granites, to 1100 µg/g in S-type and 700 µg/g in I-type (Fig. 3.9). However, the first and third quartile values of A-type and I-type granites do overlap and the total range of values is similar across all types.

Trends in Mineralogy There are several observations that arise from examining the mineralogical data. First, samples observed to contain both amphibole and mica are poorer in fluorine than rocks that contain one or the other, with median whole-rock F concentrations increasing from 1050 $\mu\text{g/g}$ in mica+amphibole-bearing to 1500 $\mu\text{g/g}$ in mica-free, amphibole-bearing rocks and 1600 $\mu\text{g/g}$ in amphibole-free, Mica-bearing rocks. Granites containing lepidolite have the highest median F content (>1 wt.%) compared to granites containing other mica species, followed by 1500 $\mu\text{g/g}$ in muscovite-bearing rocks and 1100 $\mu\text{g/g}$ in biotite-bearing rocks.

The presence of select fluorinated accessory phases also correlates with whole-rock fluorine. Apatite-bearing samples have much lower median F contents (1100 $\mu\text{g/g}$) than samples bearing fluorite (2900 $\mu\text{g/g}$) or topaz (5800 $\mu\text{g/g}$).

Discussion

Role of F in global granitic melts

Fluorinated magmas behave differently from their hydrous and anhydrous counterparts. Although whole-rock F is correlated with indicators of fractionation (e.g., decreasing MgO, increasing Rb/Sr), there are aspects of whole-rock chemistry that cannot be explained by the simple explanation that F behaves as an incompatible element during melting and crystallization. For example, the fractionation between the geochemical twins Nb and Ta is not observed in granites without significant concentrations of ligands like F. Although it is viewed as common knowledge that A-type granites have higher F contents, and this assumption is true of the averages of

the main types, both I- and S-types have overall ranges of content similar to A-type granites, and the median values for each of these three groups are within the quartiles of the other two. Despite being one of the most common F-bearing minerals, fluorapatite is not a good indicator of a highly fluorinated granite; topaz is a much better accessory mineral to use for this purpose. Similarly, rocks bearing both mica and amphibole are counter-intuitively lower in F than rocks that contain one or the other.

It is evident that, despite 60 years of study, there are still aspects of fluorine behavior in silicate melts that are poorly understood. There are many generalized assumptions (e.g., F is higher in A-type magmas) that are not as valid on a global scale as previously thought. Similarly, there are nuances in other whole-rock geochemical trends that cannot be assessed by looking at specific plutons and only arise when examining a global population (i.e., high F does not always indicate significant concentrations of HFSEs). Future work should focus on examining the relationship of mineral chemistry with whole-rock fluorine, as well as integrating investigations of natural systems with experimental work.

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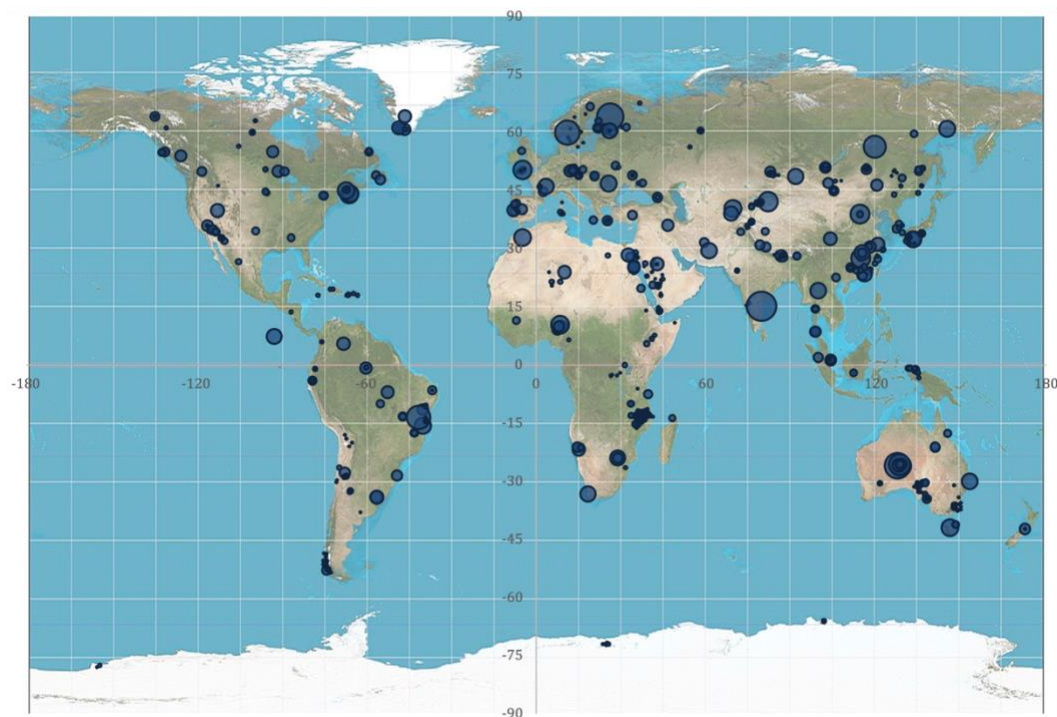
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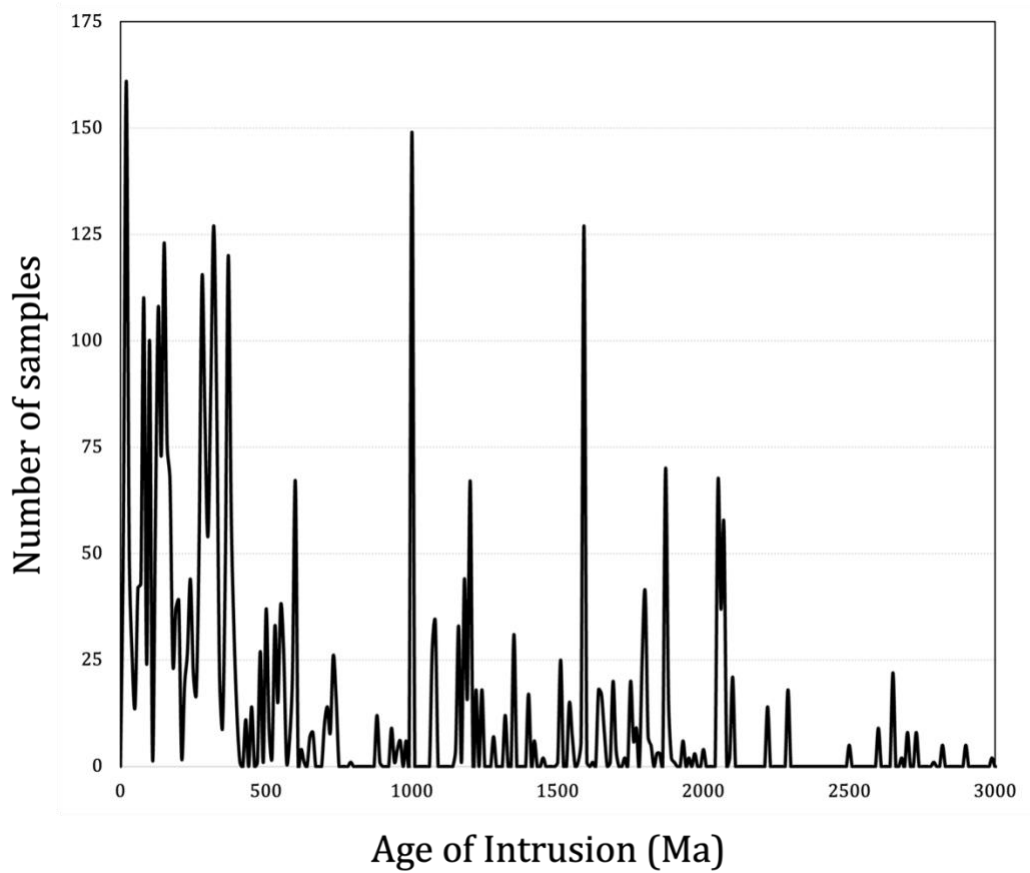
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Figures



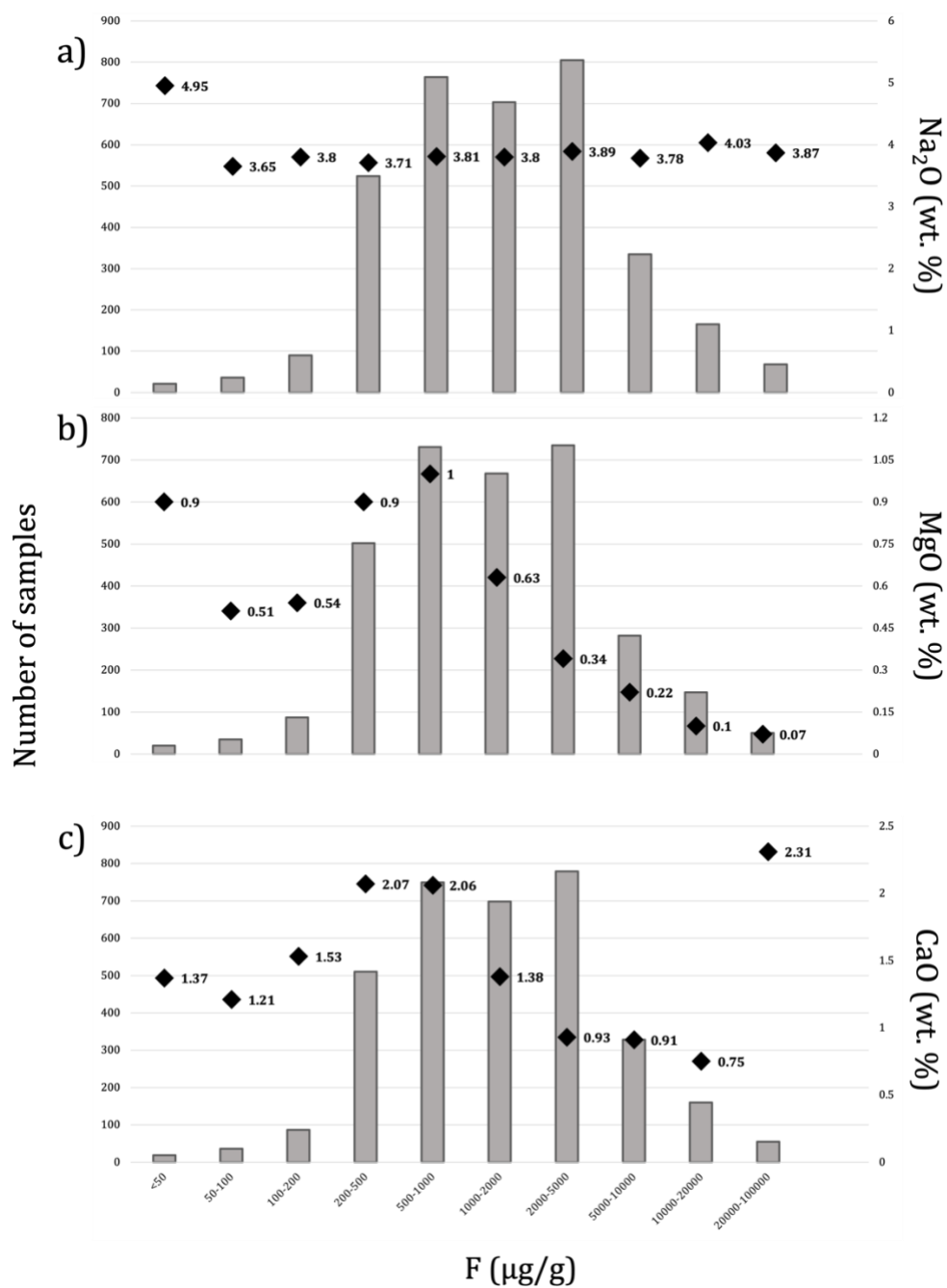
[Figure 3.1](#)— Geographic location of samples included.

Location of samples in this compilation on an equirectangular projection. The size of dots is proportional to the number of samples from a given locality.



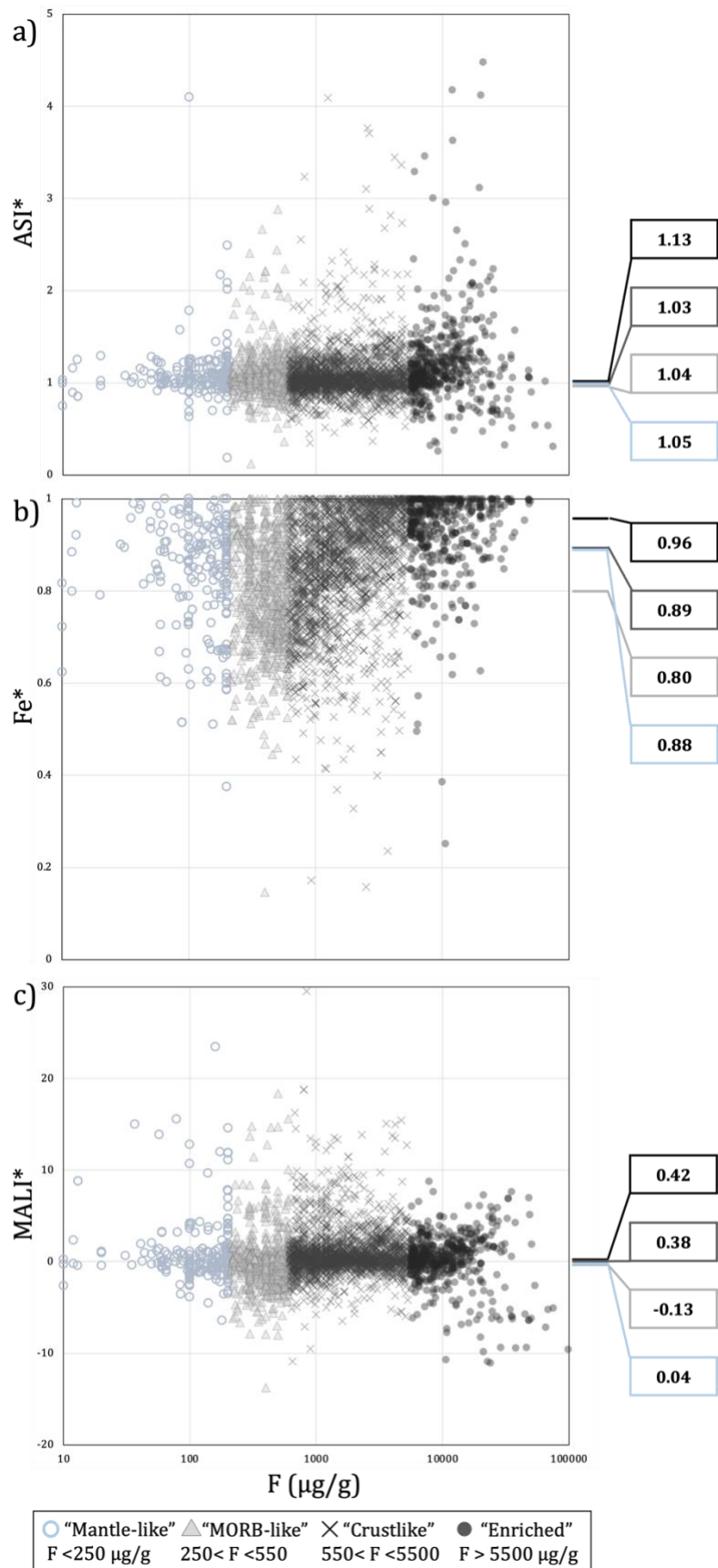
[Figure 3.2](#) – Histogram of ages of intrusions

The distribution of ages presented in this compilation (bins are 10 Ma). There are a significant number of samples from the Cretaceous (66-145 Ma, $n=555$) and the Mesoproterozoic (1000-1600, $n=520$).



[Figure 3.3](#) – Number of samples and average major elements binned by F Distribution and average of three major elements, Na₂O (a), MgO (b), and CaO (c), binned with respect to fluorine whole-rock concentrations. Histogram counts are shown on the left axis and average concentrations shown on the right axis. Na₂O does

not change with F content, MgO decreases with increasing fluorine, and CaO decreases except at extreme F concentrations. However, the behavior at extremely high and low fluorine content is reliant on a much smaller number of samples than the behavior in rocks with crust-like F. In all three cases, intermediate concentrations of F (i.e., 200-5000 $\mu\text{g/g}$) are best represented, but there are a non-negligible number of extreme samples (~500 samples with $>5000 \mu\text{g/g}$ F). The histograms are slightly different, as not every sample with reported F has corresponding data for every major element.



[Figure 3.4](#) – Granite geochemical parameters of Frost et al. (2001).

Plotted against F ($\mu\text{g/g}$) and grouped by F content: ASI* (a), Fe* (b), and MALI* (c) as defined in the text and the concentrations of F used for grouping as in Table 1 (references therein). The median value for each F-content group is presented to the right of each plot. There is no obvious change in ASI* or MALI* with increasing F, but median Fe* approaches the 1.0 ferroan limit in the high-F population.

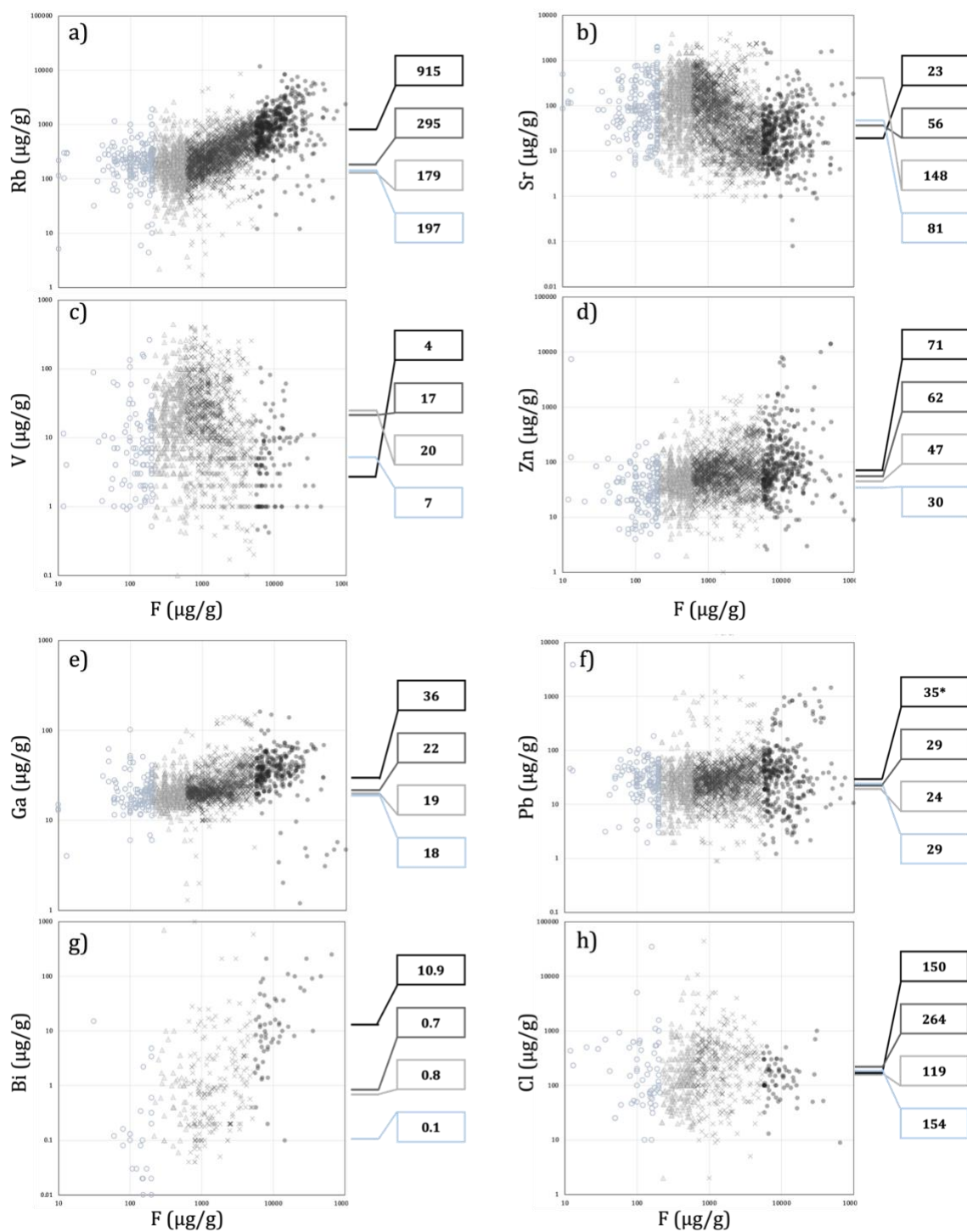


Figure 3.5 – Scatter plots of whole-rock fluorine against trace elements.

The plots are F versus Rb (a), Sr (b), V (c), Zn (d), Ga [\(e\)](#), Pb (f), Bi (g), and Cl [\(h\)](#). All plots are log-log to best show the entire range of concentrations. Symbols as in Figure 3.4 and the median value for each F range is presented to the right of each plot. The behavior of trace elements with fluorine ranges from positively correlated (Rb) to negatively correlated (Sr) to no correlation (Cl). In some cases, the scatter of samples makes visual interpretation difficult (Bi), and so the discussion in the text is partially reliant on numerical evaluations of median and average values when binned by F content. However, plots like these illustrate cases in which the median and/or average are not representative of the population due to bimodal or outlier distributions, as in the high-F population plot with Pb (f), which has a few dozen points of significantly higher Pb than the rest.

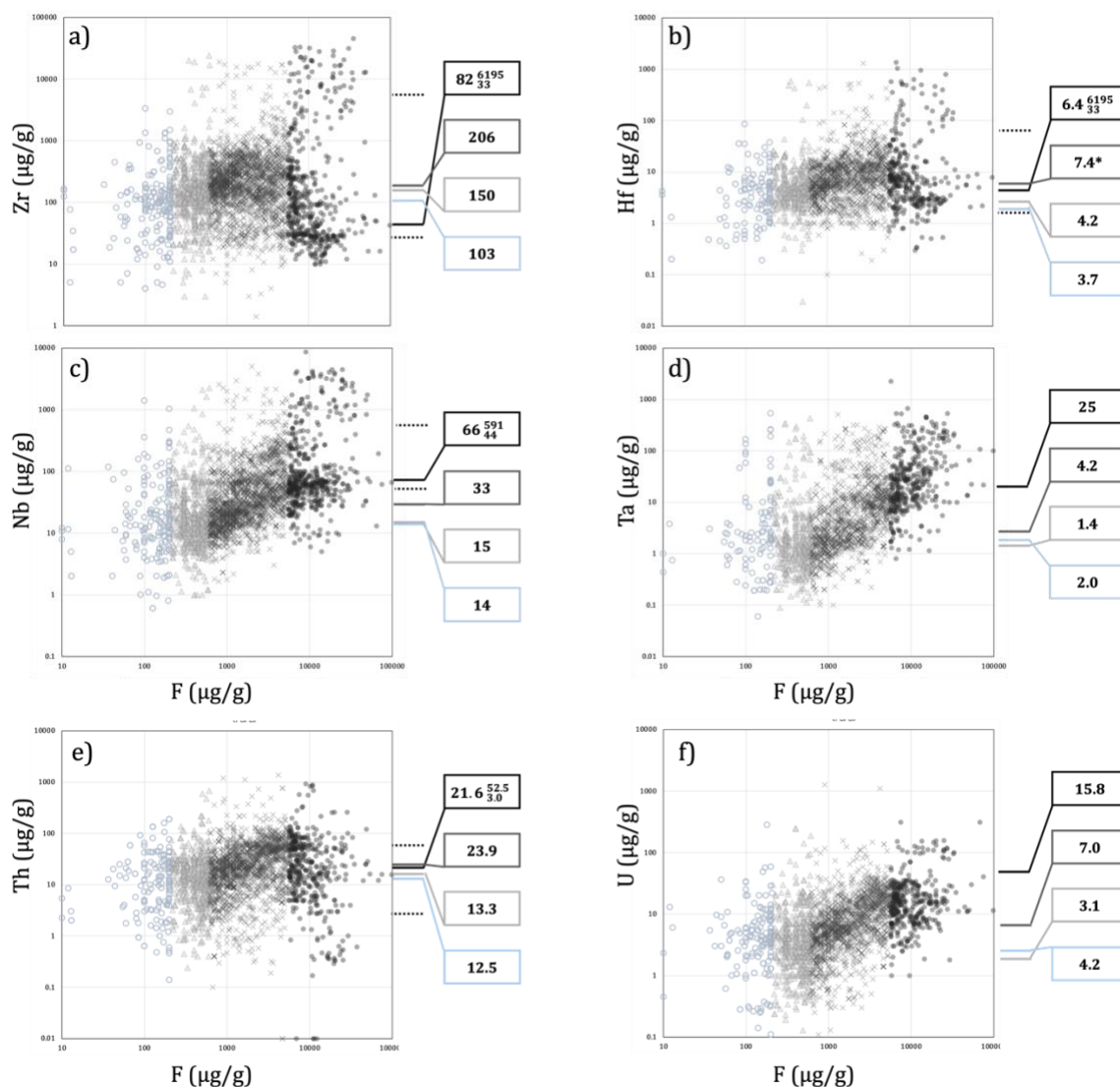
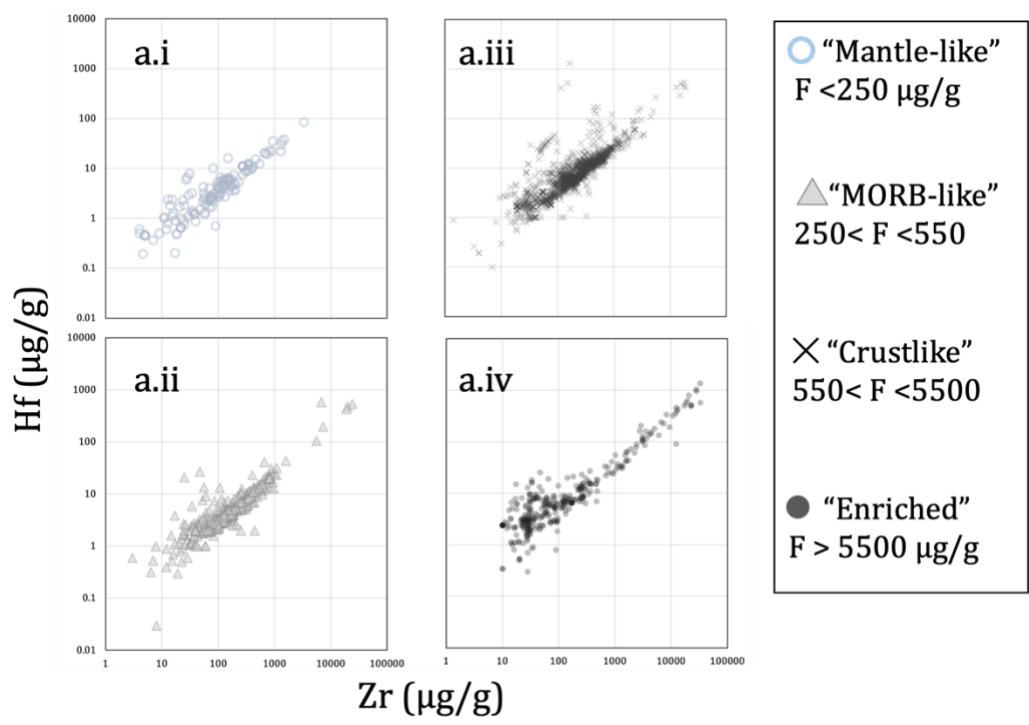
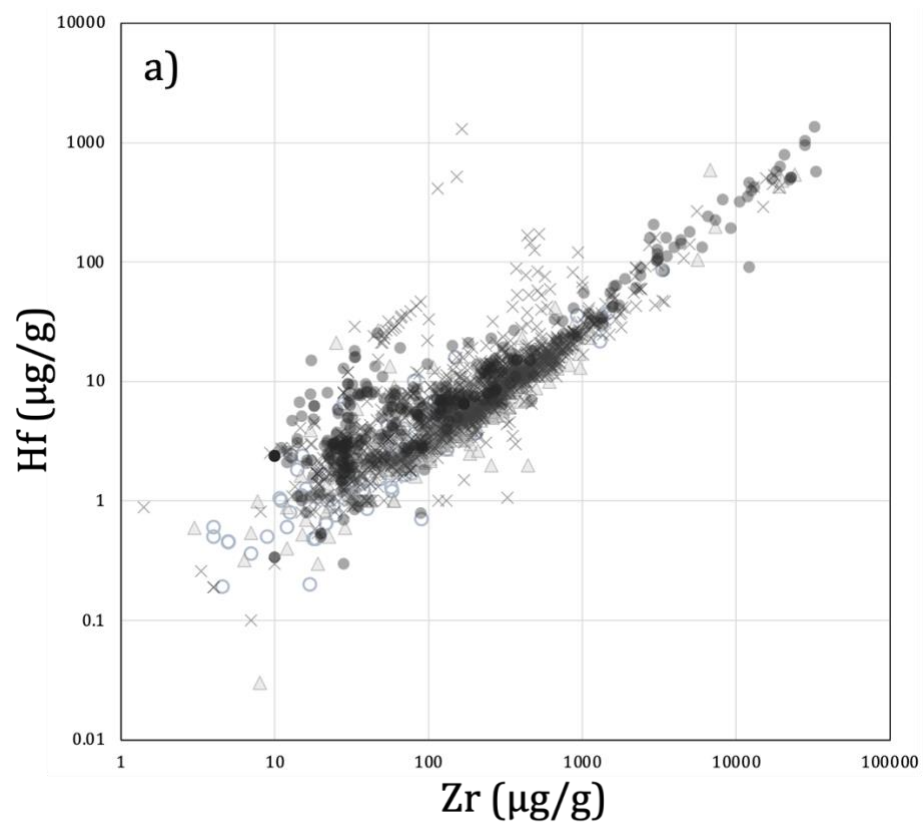
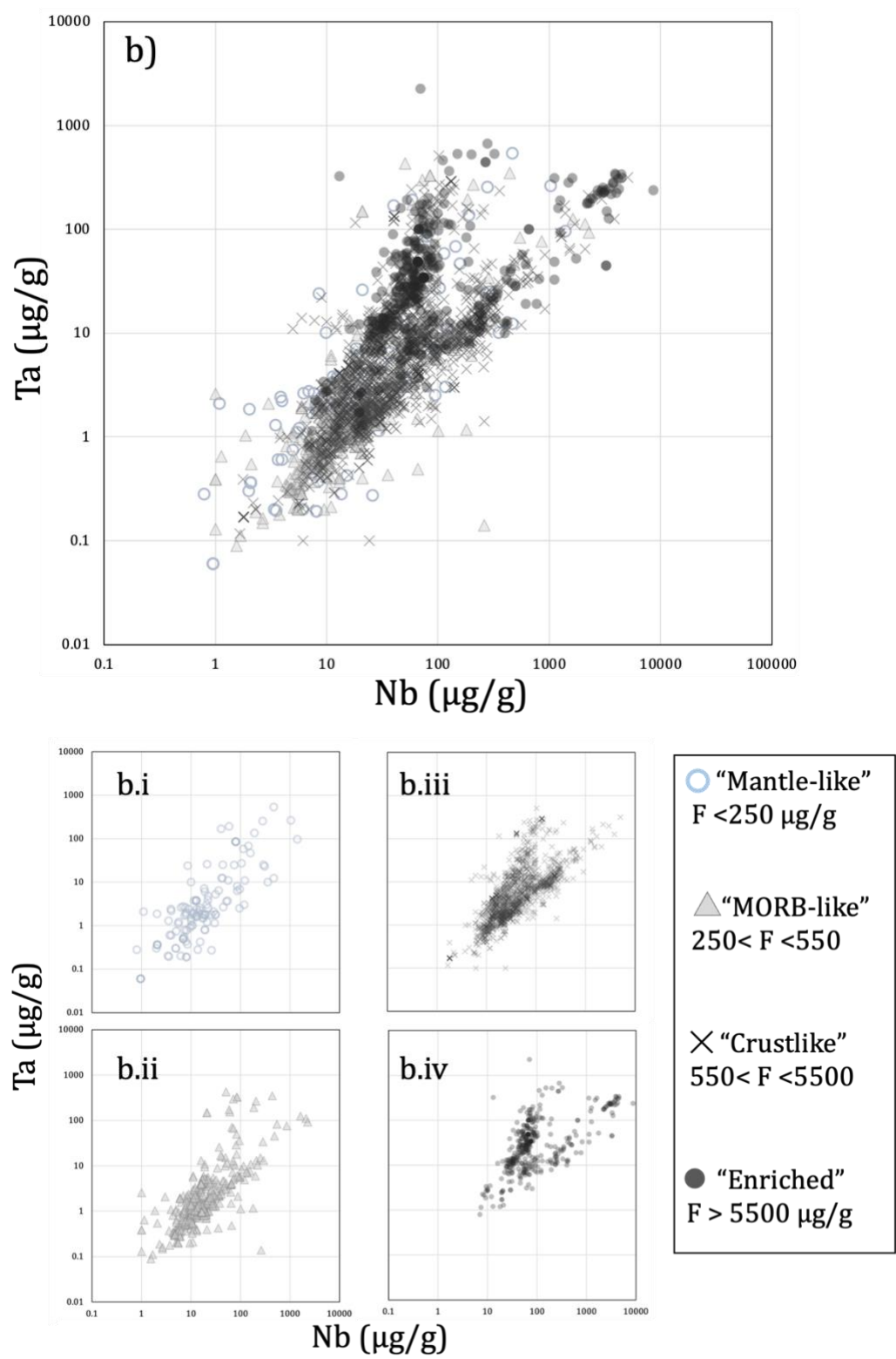


Figure 3.6 – HFSE against whole-rock F.

Scatter plots of whole-rock fluorine against Zr (a), Hf (b), Nb (c), Ta (d), Th (e), and U (f). All plots are log-log to best show the entire range of concentrations. Symbols as in Figure 3.4 and median values are presented for each F group to the right of the plot. These plots are excellent illustrations of the bimodal behavior in high-F ($F > 5500 \mu\text{g/g}$) rocks, which can be seen easily in Zr (a) and Nb (c), and are a little less resolved in Hf (b) and Th (e). The dashed lines and super-/sub- script values reference the

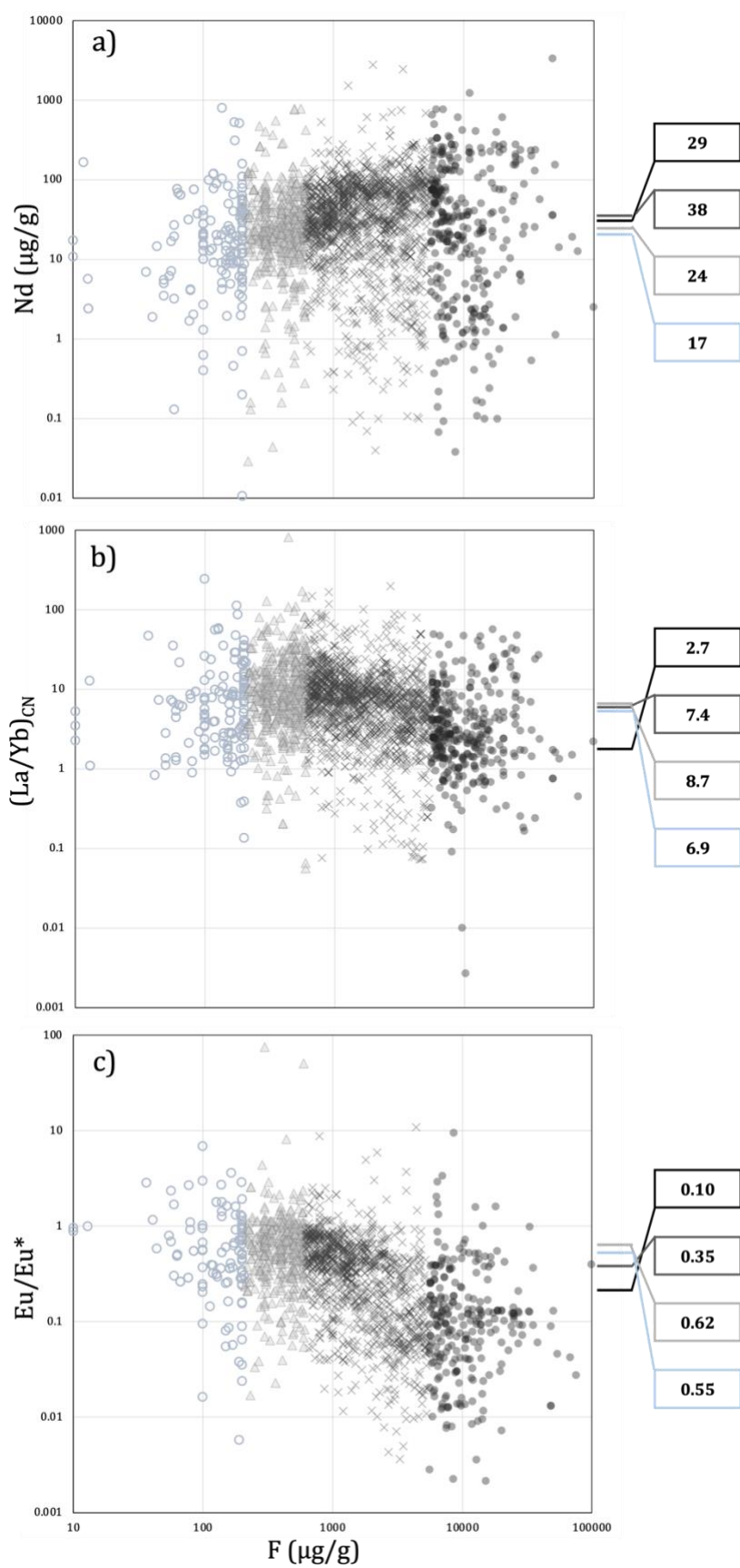
medians for the bimodal high-F groups while the solid line and main-font values are the whole group. In these four elements, the higher concentration population is made of peralkaline samples while the lower concentration samples are all strongly peraluminous. Ta (d) and U (f) concentrations are positively correlated with F across the entire range of compositions, although U also has a small discrete population of high concentration samples.





[Figure 3.7](#) – Zr, Hf, Nb, and Ta behavior with F.

The relation of geochemical twinned elements, Zr and Hf (a) and Nb and Ta (b), which are believed to behave identically under magmatic processes due to their identical charges and similar ionic radii (CHARAC). All samples are plotted together, and have been separated by their F content (i-iv), symbols as in the accompanying panel. Over all whole-rock F concentrations, Zr and Hf behave coherently (a.i-a.iv), forming a linear trend. There is a slight amount of spread in high F rocks with low Zr, but otherwise the vast majority of samples fall on an expected CHARAC trend. On the other hand when examining Nb and Ta, only samples with less than crustal F concentrations ($<550 \mu\text{g/g}$; Wedepohl 1995) show a comparable trend. At higher whole-rock F (b.iii-b.iv), there is a dramatic split in behavior, one of which continues along the CHARAC path. The shallow, CHARAC prong corresponds to the peralkaline population identified in Figure 6, and the steep, non-CHARAC population is the complementary peraluminous sample trend. Fractionation between geochemical twins is often interpreted to be the result of magmatic-hydrothermal transitions (Irber 1999; Ballouard et al., 2016), but the deviation between the pairs of twins is less understood (Aseri et al., 2015).



[Figure 3.8](#) – REE diagrams with F content.

The plots show a representative simple concentration (Nd, a), the enrichment of light over heavy lanthanides ($[\text{La/Yb}]_{\text{CN}}$, b), and the europium anomaly (Eu/Eu^* , [c](#)). The formulations and normalizing values as described in the text, and symbols as in Figure 3.4, and the medians are presented to the right of the plot for each F group. There is no obvious correlation between absolute correlation of any lanthanide or total REE content with fluorine. In a few elements, including Nd (a), there may be a poorly resolved pattern akin to the one described in Th, but it is not nearly as pronounced. There are slight and moderate trends towards lower values of $(\text{La/Yb})_{\text{CN}}$ and Eu/Eu^* , respectively, with increasing F.

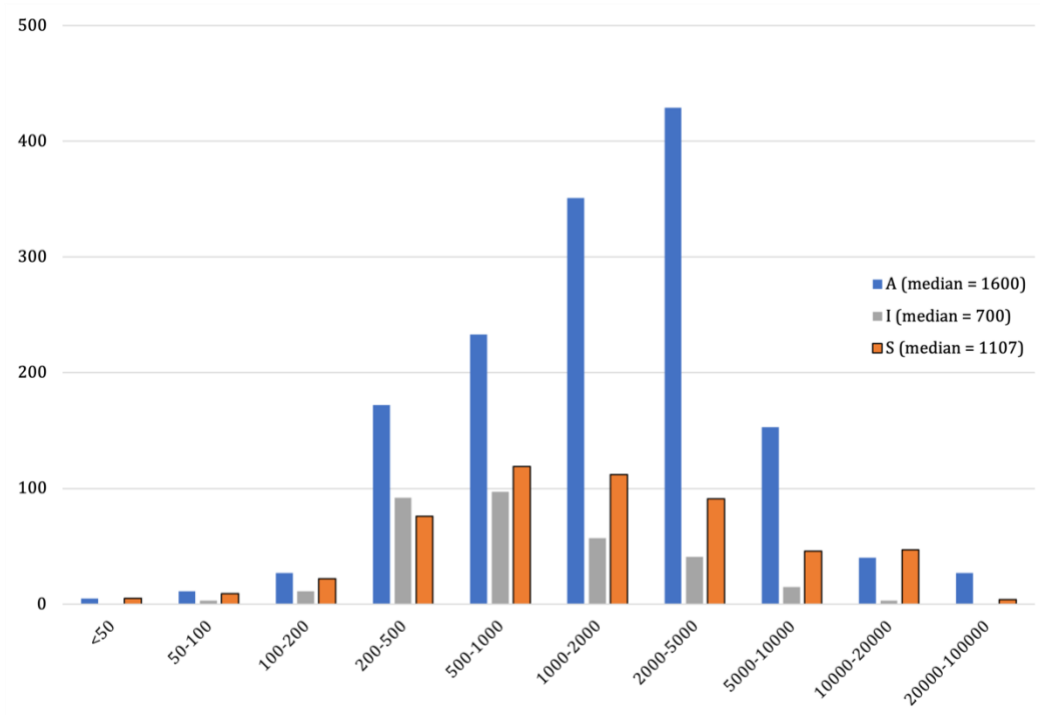


Figure 3.9 – Granite types and F content.

Histogram showing the distribution of fluorine content across the three major granite types (Chappell & White, 1974; Loiselle & Wones, 1979), binned quasi-logarithmically. Although there is a slightly higher median F in A-type granites (1600 $\mu\text{g/g}$), the margin over I-types (700 $\mu\text{g/g}$) and S-types (1100 $\mu\text{g/g}$) is not as significant nor as diagnostic as descriptions in the literature would indicate. All three types show a nearly identical total range of F concentrations, which extends from <50 $\mu\text{g/g}$ to >2 wt.% in all granite types.

Appendix III

Files in Deposit:

- **Compiled data in Supplementary Table 4.1**
- **References in Compilation in Supplementary Table 4.2**

CHAPTER IV

THE ABU DABBAB AND ABU RUSHEID FLUORINE-RICH
RARE-METAL GRANITES OF THE EASTERN DESERT OF
EGYPT

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Abstract

Many post-collisional alkaline granites in the Eastern Desert of Egypt, the northern extension of the Neoproterozoic Arabian-Nubian Shield, are distinctly enriched in rare metals. The mechanism by which these rocks formed is poorly understood, as is the observed correlation between high concentrations of rare metals and of fluorine. This study investigates whether this is simply a correlation or whether fluorine may play an active role in rare metal enrichment. We present detailed petrological, mineral chemistry, and geochemical results for two of these rare-metal granites, Abu Rusheid and Abu Dabbab. Abu Rusheid has multiple lithologies, whereas Abu Dabbab is nearly homogeneous. Bulk rock data from both localities show enrichments in high field strength element (HFSEs; Zr, Nb, Hf, Ta) concentrations of 1 to 4 orders of magnitude relative to the primitive mantle. The majority of the Abu Rusheid pluton is more enriched in rare-earth elements (average $\sum\text{REE} = 185.8 \mu\text{g/g}$) than Abu Dabbab (average $\sum\text{REE} = 31.9 \mu\text{g/g}$). Petrographic and mineral chemical data show that Abu Rusheid has a wide assemblage of accessory minerals, including rare-earth phosphates, and high F content in its minerals, namely in abundant zinnwaldite and fluorite. Abu Dabbab, on the other hand, shows strong enrichment specifically in Ta and Mo. Neither pluton can be interpreted as a purely magmatic system, as both present significant geochemical and textural evidence for metasomatic alteration. Differences in the chemistry and mineralogy of the two plutons provide evidence for multiple distinctive episodes of alteration, including infiltration by both fluorinated and fluorine-free fluids. While the results reveal relationships among F content and

HFSE concentration at multiple scales, from individual accessory grains through hand samples to alteration zones to entire plutons, they do not point to a clear causative role for fluorine in mobilizing or concentrating HFSEs.

Introduction

The Arabian-Nubian Shield (ANS) is a large tract of Neoproterozoic basement rock exposed on either side of the Red Sea that formed as a result of the collision of East and West Gondwana in the Ediacaran (e.g., Azer and Asimow, 2021). The ANS represents the northernmost part of the Pan-African Orogen and is complex in its lithology. Many of the principal units include heavily altered oceanic island arcs and ophiolites, later intruded by a variety of types of granitoid plutons throughout the active period of assembly and stabilization of the shield. Some of the currently exposed units of this suite of rocks in the Eastern Desert (ED) of Egypt include post-collisional, alkaline, A-type granites ([Fig. 4.1a](#)). These granites often host high concentrations of high field strength elements (HFSEs; Zr, Nb, Hf, Ta) and other rare metals, as well as highly fluorinated minerals (e.g., Küster, 2009; Melcher et al., 2017; Zoheir et al., 2020). Although these rare-metal granites are exposed through most of the ED, their geochemical characteristics are highly variable from one intrusion to another (e.g., Botros, 2021 and references therein). Magmatism occurred throughout the duration of the orogeny, but many of the rare-metals granites yield ages between 630 and 570 Ma (Stern and Johnson, 2010 and references therein; Johnson et al., 2011), with isotopic data suggesting recycling of the juvenile, Neoproterozoic crust (e.g., Stern et al., 2024). The origin of these postcollisional

granites is less well understood than the syntectonic intrusions, although many hypotheses have been proposed that seek to explain both their significant volume and unusual geochemical make-up (e.g., Johnson et al., 2011; Lehmann et al., 2020; Zoheir et al., 2020), including delamination of the lithosphere (Johnson et al., 2011).

Many authors have observed a correlation between concentrations of fluorine and HFSEs in these rocks (e.g., Abu El-Rus et al., 2017; Abuamarah et al., 2019; Zoheir et al., 2020; Lehmann et al., 2020, etc.). These correlations include geochemical analyses (e.g., between whole-rock concentrations of F and Nb), fluorinated mineralogy (e.g., co-occurrence of topaz and fluorite with columbite-[Fe]), and textural features (e.g., cassiterite occurring within areas of greisenization). Fluorine, a halogen, is observed experimentally to increase solubility of HFSEs in granitic melts (e.g., Aseri et al., 2015) and to promote fractionation among the lanthanides (or rare-earth elements, REEs; Irber, 1999). Proposed chemical mechanisms for this behavior include the strength of the F ion as a ligand relative to the ubiquitous oxygen ion (Bau, 1996; Farges, 1996), depression of the granitic solidus (Manning, 1981), and production of HFSE-F complexes in the melt (Keppler, 1993). However, few geochemical and petrological models have been designed to include halogens. If the presence of fluorine in a magmatic system affects the speciation and resulting behavior of HFSEs, then there is a pressing need for models to include it, and development of such models requires well-studied test cases for validation. This study aims to develop two case studies for such model validation by assembling

comprehensive whole-rock and mineralogical information about the Abu Rusheid and Abu Dabbab rare metal granites. The tools needed to form a complete interpretation of these data may not yet be available; this work aims to contribute to the development of such tools.

Both of these plutons have been investigated many times since their discoveries (e.g., Sabet et al., 1973; Hilmy et al., 1990; Mohamed 1993; Ibrahim et al., 2000; Raslan, 2005; Raslan, 2008; Raslan and Ali, 2011; Ali et al., 2011; Gippsland 2007; Lehmann et al., 2020; Zoheir et al., 2020; Sami et al 2022). Previous work occasionally yielded conflicting interpretations, particularly from Abu Rusheid, which was described as “barren” by Mohamed (1993) and “mineralized” by Ali et al. (2011). It was interpreted as a “metapelite” by El-Ramly et al. (1984), as a “gneiss” by Raslan (2008), and as a “sheared granite” by Ibrahim (2000). Despite repeated study, a number of minerals are mentioned in only one published description of the plutons — at Abu Dabbab, sphalerite and microlite are described only by Zoheir et al. (2020), apatite and native copper are reported only by Abuamarah et al. (2021), and thorite is only observed by Sami et al. (2022). These literature disagreements demonstrate that a broader, more comprehensive examination of the plutons is necessary. In addition to investigating the behavior of fluorine, this study provides a more thorough description of the complete mineralogy and petrologic features of both plutons.

After introducing the geologic setting of the studied plutons, we describe our sampling and analytical strategy, which includes several innovations. Volatile

elements (F, Cl, S) that are difficult to analyze by either conventional fused bead X-ray fluorescence or solution-source plasma ionization mass spectrometry were analyzed by laser ablation of pressed pellets. Accessory phases with high concentration of elements that may be present in the whole rock at trace levels were analyzed with an extended wavelength-dispersive electron probe protocol. The petrographic, whole-rock, and mineral chemical data are applied to constrain the magmatic and post-magmatic processes that affected each pluton. We close with an interim assessment of the influence of fluorine on the development of rare-metal granites.

Geologic Setting

Following the rifting of supercontinent Rodinia in the Neoproterozoic, the Mozambique Ocean opened, forming spreading centers and subduction zones. Around 750 Ma, the ocean began to close, creating arc-related deposits and obducting pieces of the oceanic crust onto the margin of East Gondwana (Stern, 1994; Abdelsalam and Stern, 1996; Stern and Johnson, 2010; Johnson et al., 2011; Johnson, 2021 and references therein). This collision ceased around 600 Ma and was followed by extensive post-collisional calc-alkaline and alkaline volcanism and intrusions, continuing until about 570 Ma, with minor intrusive activity until 540 Ma (Fig. 4.1; e.g., Stern and Ali, 2020; Abuamarah et al., 2021). Until the opening of the Red Sea rift, these rocks underwent little in the way of tectonic deformation or alteration after their emplacement, and so they provide an excellent window into the Pan-African Orogeny.

Some of the post-orogenic plutonic rocks are well-exposed in the ED of Egypt and the origin of these rocks are highly debated, as post-collisional rocks are difficult to explain within the paradigm of plate tectonics (e.g., Zoheir et al., 2020; Azer and Asimow, 2021). One of the prevailing hypotheses invokes the delamination of the lower lithosphere, which then causes an influx of hot asthenosphere and leads to melting of the lower crust (Avigad and Gvirtzman, 2009). This is supported by evidence that the shield experienced several kilometers of isostatic uplift followed by a significant erosional event after the collision. A key issue that this class of models leaves unsettled is the extent to which new mantle-derived magmas or fluids were added to the crust, along with or as a mechanism of heat transfer. Isotopic indicators of juvenile mantle material in the post-collisional stage have proven ambiguous because the ANS crust was so young at the time (Morag et al., 2011; Sami et al., 2022), though recent work by Stern et al. (2024) has been more successful. These granites have received significant attention due to their enrichment in rare metals and other economically valuable elements (e.g., Gippsland Ltd., 2007; Küster, 2009).

Two of these granites are the Abu Rusheid and Abu Dabbab intrusions ([Fig. 1b and 1c](#)). Abu Rusheid (24°40'30"N, 34°46'01"E) is exposed as a 30 km² elongated intrusion into ophiolitic mélange country rock in the southern ED (Ibrahim et al., 2000; Ibrahim et al., 2004; Raslan and Ali, 2011). The pluton is made up of zones of foliated granite and garnet-bearing leucogranite, with localized areas of granodiorites and adamellites. Three washes (*wadis*) surround the intrusion, Wadi Nugrus (Saleh,

1997), Wadi Abu Rusheid (Hassan, 1973), and Wadi Sikait (Stern et al., 2024). The lithologic boundaries of the pluton with the country rock are described as sharp structural contacts. This pluton is moderately to heavily altered and strongly foliated in some outcrops (Raslan and Ali, 2011), to the point that some authors have interpreted the foliated rocks as gneisses (e.g., Ali et al., 2011). A better interpretation that reflects the texture as well as the primarily igneous character of the rocks is foliated or “gneissose” granites. Abu Rusheid has been the focus of several studies due to its uranium and columbite mineralization, most pronounced in the more altered units (Ibrahim et al., 2000; Hilmy et al., 1990; Raslan, 2005, 2008). Yet studies that have focused on the bulk of the intrusion, away from the altered zones, have described it as a barren pluton (Mohamed, 1993). The lithologies present in this pluton include the main body of foliated granite and lesser amounts of garnet-bearing granite and leucogranite. The boundaries between the main, sheared body and other units, including the leucogranite and the country rock are sharp, not gradational ([Supp. Fig. 4.1a, b](#)). An attempt at dating monazite within this pluton resulted in an age of 629 ± 5 Ma (Ali et al., 2011). However, that study assumed no fluid had interacted with the sample. A more recent study determined a similar U-Pb age of 629.3 ± 14 Ma using SIMS to measure zircon (Stern et al., 2024), although the authors report that the small number, heterogeneous degree of radiation damage, and inclusion-rich character of the analyzed zircon grains leaves some ambiguity in the measured age.

Further north in the central ED, the Abu Dabbab pluton (25°20'45"N, 34°32'35"E) intruded into metavolcanic and metasedimentary host rocks around 644 Ma, making it one of the oldest granite intrusions of this suite in the ANS (Abuamarah et al., 2021; Lehmann et al., 2020). It is an ellipsoidal stock, slightly elongated in the E-W direction with a small offshoot to the northwest. It is one of the smaller post-collisional plutons, with an exposed area of ~50,000 m². It consists of fine- to medium- grained leucogranite. The northeast margin of the pluton is bounded by a northwest-southeast trending sinistral strike-slip fault, while the remaining margins are intrusive contacts, marked by stockscheider pegmatites along the southern margin (Abuamarah et al., 2021). Most previous authors report no xenoliths, mafic enclaves, or dikes within the body (Abuamarah et al., 2021; Sami et al., 2022), although some previous studies described extensive cross-cutting by quartz veins (Heikal et al., 2019). Alteration within the pluton has been invoked to describe the albitization of its feldspars, Mn-oxide clusters, and abundant greisen (Supp. Fig 4.1d; Khedr et al., 2023). Abu Dabbab is well recognized for its high-grade mineralization of Ta and possibly significant resources of Sn (Gippsland Ltd., 2007; Küster, 2009; Melcher et al., 2015).

Analytical Techniques

Whole rock

One hundred samples were collected from Abu Rusheid (series ARS, 1014, Skt, NgR, and Ard) and 29 from Abu Dabbab (series AD and Adb). Numerous rock types are represented, including the granitic plutons, associated veins or dikes, and non-

granitoid country rocks. The majority of samples were collected from exposures in the walls of the wadis, although two drill cores were obtained by the Archean for Geological and Mining Services company from the sheared portion of Abu Rusheid (Supp. Fig. 4.1c; series ARS and 1014). The drill core samples are subdivided into near-surface and sub-surface groups; the sub-surface samples are ARS10A-E and 1014 F-J.

At the California Institute of Technology, samples were chipped in a WC jaw crusher and ground in an agate ball mill. One aliquot of each sample was fired in air at 1000 °C for one hour to determine loss on ignition (LOI), and fused with ten times its mass of lithium borate flux to create a glass bead. These fused beads were then analyzed for major elements with a Panalytical Zetium wavelength-dispersive (WD) X-ray fluorescence (XRF) system using a calibration protocol based on a large set of USGS reference materials. The samples were bracketed by measurements of USGS standards AGV-2, BCR-2, RGM-2, and GSP-2 for quality control. Following XRF measurement, a 25 ± 1 mg shard of each bead was placed in a new polypropylene tube and dissolved in 2 mL of a 3:1 mixture of hydrofluoric and nitric acid at 95 °C for at least 5 hours. After being brought to dryness, the samples were resuspended in 10 mL of a dilute solution of 5% nitric and 0.1% hydrofluoric acid at 50 °C for one hour before being brought to a final volume of 30 mL with the same dilute acid solution. A set of 34 trace elements were then analyzed with an Agilent Technologies 8800 Triple Quadrupole inductively-coupled plasma mass spectrometer (ICP-MS) in

helium mode. This protocol involves using four in-house standard solutions to create a four-point calibration curve for each element, along with a similarly prepared, in-house quality control measured after every eighth sample. Analytical conditions, detection limits, and quality control indicators are provided for the fused-bead XRF and ICP-MS measurements in the Supplementary Information.

Additional whole-rock measurements were conducted on pellets pressed from unfired sample powders to obtain bulk concentration of elements that are lost during ignition and fusion. For halogen and sulfur measurements, 13 mm diameter pellets were pressed from intimately mixtures of 330 ± 1 mg of finely ground powder and 70 ± 1 mg of cellulose binder. These pellets were analyzed by WD-XRF with a calibration protocol analogous to that for the fused beads (Wilner et al., 2025). Details of this novel procedure, with calibration and analytical conditions, are included in the supplementary information.

Details regarding the analytical conditions, detection limits, and certification of data quality for all methods is provided in the Supplementary Information. All analyses were conducted at the California Institute of Technology.

Mineral Analyses

All 129 samples were prepared as polished thin sections. Twenty-two samples (series ARS, 1014, and AD) were made into 1” round polished thin sections, while the remaining 107 samples were made into 27x46 mm rectangular sections. Thin sections

were initially photographed in reflected and transmitted light. Following application of a carbon-coat, all samples were investigated with a Zeiss 1550VP Scanning Electron Microscope (SEM) using both back-scattered electron (BSE) images and energy-dispersive X-ray analyses to identify regions and phases for further analysis. The 1" round sections were analyzed with a JEOL JXA-8200 electron microprobe (EPMA) and, following a laboratory upgrade, 90 of the rectangular sections were analyzed with a field-emission source JEOL iHP-200F EPMA. An extended suite of elements (F, Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Y, Zr, Nb, Sn, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Hf, Ta, Pb, Th, and U) were analyzed with a 25 nA beam current, 15 kV accelerating potential, and a $\sim 1\text{ }\mu\text{m}$ focused beam. Specifics of this analysis protocol, including standards, interference corrections, choice of X-ray lines and diffracting crystals, detection limits, accuracy checks, and analysis times, are provided in the Supplementary Information and Supp. Table 4.1. We are aware that analysis of such normally trace-level elements by EPMA is unusual practice; here it is suitable because the elements of greatest interest are in most cases concentrated to weight percent (or greater) levels in minor accessory phases and therefore easily detected and quantified at microscale by EPMA. The combination of high spatial resolution and high spectral resolution makes this technique more quantitative for these accessory phases than laser ablation or SEM-EDS.

Some spots with inconclusive phase identifications were confirmed by collection of Raman spectra on a Renishaw inVia Raman spectrometer, with mineral identity

determined by matching to X-ray analyzed standards from the RRUFF database. Raman protocols and conditions are described in the Supplementary Information. Microscopy, SEM, EPMA, and Raman analyses were conducted at the California Institute of Technology.

Results

Mineralogy and Petrography

The primary mineralogy of the granitoid thin sections is similar from both localities, with the most abundant phases being quartz (Qtz), plagioclase feldspar (Pl), potassium feldspar (Kfs), and micas. All 129 annotated thin sections are provided in the Supplementary Material.

Quartz At Abu Rusheid, the foliated granite displays Qtz aligned with the fabric of the rock as thin (~1 mm) strings of many anhedral to interstitial crystals, making up about 40 vol.%. In the garnet granite, Qtz is larger, with individual anhedral to subhedral crystals up to 3 mm across in addition to interstitial grains, about 30 vol.%. Qtz is almost absent from some of the aplite samples, but dominates several veins, with individual, subhedral crystals up to 5 mm. The larger crystals are all heavily fractured and contain inclusions of many different phases. At Abu Dabbab, Qtz is variable in size distribution within the single lithology present, generally 25 vol.%. Qtz ranges from small (<1 mm) interstitial grains up to large (~5-8 mm) subhedral to euhedral single crystals. The larger crystals show ‘snowball’ textures, with their inclusions of feldspars and other phases aligned with growth faces ([Supp. Fig. 4.2a](#)).

Quartz at both localities contains fluid inclusions. At Abu Dabbab, inclusions are extremely abundant and range from sub-micron to $\sim 5 \mu\text{m}$ in diameter, the larger size having inverted crystal shapes (Supp. Fig. 4.2d), while at Abu Rusheid, the population of fluid inclusions are sub-micron and arranged in planar arrays interpreted as healed cracks grains (Supp. Fig. 4.2e) that in some cases cross multiple grains (Supp. Fig. 4.2f).

Plagioclase feldspar At both localities, Pl makes up a substantial fraction of the rocks (35 vol.% at Abu Rusheid, 55 vol.% at Abu Dabbab). Leucogranite samples from both localities predominantly have small, anhedral to interstitial plagioclase grains that are massive in appearance, with abundant albite twinning (Supp. Fig. 4.2b). Within the foliated granite, Pl aggregates are thin and stringy, aligned with the rock fabric. Some larger grains can be found in the veins and aplite samples from Abu Rusheid, reaching up to 5 mm across, though these larger grains are also anhedral. Pl is more abundant in the garnet granite, up to 55 vol.% of the rock. There is substantial alteration along grain boundaries in some samples to a fine-grained material, likely sericite, present at both plutons, but the cores appear to be crystalline. Pl contained within snowball quartz at Abu Dabbab (Supp. Fig. 4.2a) does not show altered rims.

Potassium feldspar Microcline, identified by tartan twinning (Supp. Fig. 4.2c), is present at both localities. At Abu Rusheid in the foliated granite, Kfs forms aligned massive bands with thicknesses less than 2 mm, comprising about 20 vol. % of the rock, while in the garnet leucogranite, grains are rarer, individual subhedral to

anhedral crystals, making up less than 10 vol. % of the sample. In the vein and aplite samples, crystals reach up to 8-10 mm, though they are still subhedral in character. At Abu Dabbab, Kfs is generally euhedral to subhedral and 2-5 mm across, with some interstitial grains in the finer grained samples. The largest crystals are usually associated with the large Qtz crystals noted above. At both localities, large Kfs grains are very rich in inclusions. Fluid inclusions in Kfs at Abu Rusheid are rare and small ($<1\ \mu\text{m}$), but at Abu Dabbab, they are common, small ($\sim 1\ \mu\text{m}$), and occur in arrays parallel to tartan twin sets (Supp. Fig. 4.2e). As with plagioclase, there are rims of alteration around many grains, as well as precipitates of Fe-rich phases in cracks within the grain cores (Supp. Fig. 4.2e).

Micas In thin section, dark and light micas are present as interstitial or sub-mm grains, although both localities display a tendency for the micas to form ‘clots’ or highly micaceous aggregates. At Abu Rusheid, these clots can be large enough to form hand samples (e.g., NgR 22) with individual grains up to 1cm across, while at Abu Dabbab, the clots reach 3-4 mm in size with sub-mm grains. The garnet granite is the most micaceous lithology after the greisen and clots, with at least 8 vol. % total micas, followed by the main body granites from both locations with ≤ 5 vol. %. Micas of all compositions from both localities are frequently inclusion rich or have grown around rare-metal phases (e.g., [Fig. 4.2a](#)).

Garnet Grt was primarily observed in samples from Abu Rusheid, although one sample from Abu Dabbab contained a garnet-lined fracture (Sami et al. 2022). All

garnets are heavily fractured (Fig. 4.2b). Those visible in hand sample are dark red and the size range spans from ~0.5 mm up to 5 mm.

Zircon Zrn is rare at Abu Dabbab and was only observed in nine samples. All of these samples showed very small (<80 µm), highly angular and euhedral crystals, all of which are inclusion-free (Fig 4.2a). Frequently, many small (~10 µm) crystals appear in a cluster within a major phase, like quartz or mica. Abu Rusheid, on the other hand, has large and abundant Zrn. Crystals range from 10 µm up to 1 mm across, and are usually rounded, though some are subhedral (Fig. 4.2d). They are very rich in inclusions and have complex morphologies, with many cracks and fractures, as well as evidence for multiple episodes of growth seen in the orientation of inclusions, profiles in chemistry, and CL imaging ([Fig. 4.3c-d](#)). Garnet-bearing samples from Abu Rusheid exclusively show small and rare Zrn.

Fluorite Flr is a minor accessory phase in both plutons. It is usually present as inclusions within major or minor phases, as interstitial grains, or as void-filling masses (Fig. 4.2c). In all cases, the grains are small (<20 µm) and the larger aggregates (<100 µm) show fractures. In CL, Flr shows minimal zoning.

Columbite-Tantalite Group Both localities have accessory columbite. As with zircon, many of the grains at Abu Dabbab are small (60-200 µm) and euhedral, while those at Abu Rusheid are larger (100-500 µm) and rounded, almost ‘blobby’ in shape. Both

localities have odd, ‘embayed’ crystals suggesting replacement of columbite by other phases (Fig. 4.2f). The larger crystals frequently contain inclusions.

Cassiterite The morphology of cassiterite is similar in the two localities, although cassiterite in some samples from Abu Dabbab is slightly more angular. Grains range from 10 to 300 µm across, are very rounded, and have many inclusions of Qtz and other accessory phases.

Additional phases The two plutons are observed to have many opaque and trace phases that could only be identified by EPMA and/or Raman spectroscopy. Both granites contained monazite-(Ce), bastnäsite-(Ce), fluocerite-(Ce), florencite-(Ce), topaz, beryl, and thorite. Many samples, especially those collected from the surface, also contain alteration products like mixed Fe and Mn oxides, chlorite, goethite, and kaolinite. At Abu Rusheid, additional phases include: fluorapatite, galena, pyrite, chalcopryite, chalcocite, uranothorite, coffinite, pyrochlore group minerals, niobian rutile, carlosbarbosaite, euxenite-(Y), aeschynite-(Y), ishikawaite, samarskite-(Y), fergusonite-(Y), and britholite group minerals. See Supplementary information for additional detail of the Nb-Ta oxides (supplementary text; [Supp. Fig. 4.3](#)). Additional alteration products at Abu Rusheid include baryte, jarosite, gypsum, and very hydrated anglesite. Granite samples from Abu Dabbab contain tourmaline (likely rossmanite) and microlite group minerals, as well as Fe-, Mn-, and Ca- carbonates in the altered products.

Samples identified from field description, hand sample, thin-section, and whole-rock chemistry as country rocks are described in the supplement, along with more detail on the aplites and monomineralic samples.

Whole Rock Geochemistry

The bulk rock analyses for each sample are listed in Supp. Table 2 for the whole series along with the average of just the granite samples in each series. It should be noted that the whole rock data do not discriminate the rock types satisfactorily, and a more accurate determination is possible by petrographic study (see Mineralogy results). Additional information, including LOI, weathering and chemical indices, and various geochemical parameters, are also provided in Supp. Table 2.

Major Elements In the granites from Abu Rusheid, samples showed generally high and variable SiO_2 (70.1-77.8 wt. %), Al_2O_3 (9.61-16.6 wt. %), K_2O (1.09-5.50 wt. %), and Na_2O (1.96-6.36 wt. %). On average, these samples also contain very low TiO_2 (<0.04 wt. %), MgO (<0.03 wt. %), MnO (<0.10 wt. %), and P_2O_5 (<0.01%). Fe_2O_3 and CaO are both generally low in concentration but span a significant range, 0.05-3.60 wt. % (Fig. 4.4b) and <0.01-1.61 wt. % respectively. Note that these ranges exclude samples identified in hand sample to be quartz veins or aplitic dikes. The granitoids from Abu Dabbab are similar to those from Abu Rusheid in SiO_2 , Na_2O , K_2O , Al_2O_3 , MgO , P_2O_5 , and MnO content. However, the Abu Dabbab pluton has lower concentrations of Fe_2O_3 (0.17-0.57 wt. %) and CaO (0.03-0.19 wt. %). It also has a much narrower range for most major elements, reflecting the relative

homogeneity of the much smaller pluton. Both the Abu Rusheid and Abu Dabbab granitoids are strongly peraluminous ([Fig. 4.4c](#)), with aluminum saturation index (ASI; Supp. Table 2]) values spanning 1.42-2.13 and 1.41-1.82, respectively. This determination is corroborated by the presence of multiple micas, topaz, and/or garnet (see **Mineralogy** results). Despite their low Fe contents, the effective absence of Mg from these samples mean that both plutons are definitively ferroan ($Fe^* > 0.95$; Frost et al., 2001). No major elements show significant trends with SiO₂ content (e.g., [Fig. 4.4b](#)).

Trace Elements Trace element data for all samples are listed in Supp. Table 2. As with the major elements, samples identified as monomineralic veins are described in the supplement and are not included in the ranges presented here. Both plutons are highly fluorinated and enriched in F relative to continental crust (~600 µg/g; Wedepohl, 1995), with an average concentration of 2700 µg/g in Abu Rusheid granites and 3260 µg/g in Abu Dabbab granites ([Fig. 4.4a](#)). There is a significant range of F concentrations at both plutons, from <115 to 11,160 µg/g at Abu Rusheid and from 730 to 8200 µg/g at Abu Dabbab. Analyses of many trace elements (e.g., Rb, Zr, and Nb) from Abu Rusheid divide into two populations: a set of low concentration samples (e.g., ≤ 500 µg/g Zr) and a set of high concentration samples (e.g., ≥ 1000 µg/g Zr). These populations generally correspond with sample lithology (e.g., garnet-bearing, main body, etc.). When plotted against SiO₂, concentrations in the depleted population are independent of SiO₂ but the more enriched population

demonstrates trends (Fig. 5, left column), including inverse linear relationships between SiO₂ and the concentrations of Rb, Nb, and Cs. Other elements — including Sr, Ba, Th, and U — form a peaked distribution with elevated concentrations in the middle of the SiO₂ range. F shows a mildly linear positive correlation with SiO₂.

At Abu Dabbab ([Fig. 4.5](#), right column), there is a single population of trace element concentrations and only Rb yields a slight (negative) correlation with SiO₂. Other elements, including Zr (<113 µg/g Zr), Nb, Th, and U, lack the highly enriched group found at Abu Rusheid and do not indicate any correlation with SiO₂.

Normalized multi-element (spider) diagrams for trace elements and lanthanides, normalized to primitive mantle and chondrite, respectively, are shown for both plutons in [Figure 4.6](#) (McDonough and Sun, 1995). These graphs emphasize the heterogeneity of Abu Rusheid and the homogeneity of Abu Dabbab as well as the large magnitudes of the enrichments in some elements and of inter-element fractionations. These trace element patterns are discussed in more detail below.

Mineral Chemistry

Detailed chemistry of all phases is presented in Supplementary Table 3. Unless otherwise specified, all mineral chemistry concentrations were determined by EPMA.

Quartz Quartz contains up to 1.3 wt. % Y₂O₃ at both localities. The analytical totals of Qtz from both plutons are occasionally low (<95 wt. %), possibly due to placement

on near-surface fluid-inclusions. Ti was below detection limits in all but one sample, and the majority of grains had resolvable fluorine.

Plagioclase feldspar At both localities, Pl is near end-member albite ($An_{<5}$) with CaO contents generally below detection limits (<0.02 wt. %). A few samples from both plutons have quantifiable lead (PbO up to 0.65 wt. %).

Potassium feldspar As with the plagioclase feldspar, Kfs is near end-member in composition, with average Na₂O contents of 0.29 wt. % and CaO contents below detection limits (≤ 0.02 wt. %). Many of the samples from Abu Rusheid are quintessential ‘pink’ granites, supported by FeO* contents up to 3 wt. % in the Kfs (Hofmeister and Rossman, 1984), and a few samples with large crystals display amazonite, though Pb contents were below the (rather high) detection limits in all Kfs (<0.55 wt. %).

Micas The micas present are predominantly muscovite (Ms) and a fluorinated, siderophyllite-polyolithionite solid-solution known as zinnwaldite (Znw), with lesser amounts of annite, phlogopite, and, in one sample from Abu Rusheid, paragonite. The average composition of Znw from Abu Rusheid is $(K_{0.87}Na_{0.02})(Li_{1.35}Al_{0.78}Fe_{0.79}Mn_{0.05}Ti_{0.01}Zn_{0.01})(Al_{1.11}Si_{2.89})O_{10}(F_{1.14}(OH)_{0.86})$; the presence of abundant Li was confirmed by laser-ablation ICP-MS in sample 1014D (see Supplementary Information) and so Li in the structural formula was inferred from stoichiometry and EPMA analyses of other elements. Generally, micas at Abu

Dabbab are Fe-poor, mainly Ms and polyolithionite, while Fe-rich Znw dominates Abu Rusheid. Overall, Abu Rusheid shows greater heterogeneity in mica composition, though both localities display more than one mica in most samples ([Supp. Fig. 4.4](#)). At Abu Dabbab, Znw shows rims of fluorine-free Ms (e.g., Fig 2a).

Garnet At Abu Rusheid, the chemistry indicates that these is an almandine-spessartine solid solution, with some samples very Fe-rich and others with subequal Fe and Mn contents. The average Fe-rich composition is $(\text{Fe}_{2.21}\text{Mn}_{0.42}\text{Ca}_{0.39})\text{Al}_{1.98}(\text{Si}_{0.99}\text{O}_4)_3$, which has a notably high Ca content for these Ca-poor rocks, and the average composition for the Alm-Sps garnets is $(\text{Fe}_{1.73}\text{Mn}_{1.06}\text{Ca}_{0.15})\text{Al}_{1.98}(\text{Si}_{0.99}\text{O}_4)_3$. The single garnet found at Abu Dabbab (sample ADb25) was much more spessartine-rich, with an approximate composition of $(\text{Fe}_{0.4}\text{Mn}_{2.6}\text{Ca}_{<0.1})\text{Al}_2(\text{SiO}_4)_3$ determined by SEM-EDS.

Zircon Zrn from Abu Dabbab is extremely Hf-rich (~18 wt. % HfO_2 ; [Fig. 4.7a](#)) and is classified as hafnian zircon, with an idealized composition of $(\text{Zr}_{0.7}\text{Hf}_{0.3})\text{SiO}_4$. However, there are many impurities, including high abundances of F, P, Ca, Al, Th, and U, as well as hydration indicated by low analytical totals (e.g., Abd El-Naby, 2024), resulting in a true average composition of $(\text{Zr}_{0.62}\text{Hf}_{0.23}\text{Ca}_{0.06}\text{U}_{0.02}\text{Th}_{0.02})(\text{Si}_{0.91}\text{Al}_{0.05}\text{P}_{0.04})\text{O}_{3.62}\text{F}_{0.18}(\text{OH})_{0.20}$. The low totals and high fluorine contents (~1.5 wt. %) indicate that none of the zircon studied here would be suitable for dating, which is supported by the lack of cathodoluminescence (CL) in all examined zircons from Abu Dabbab (Fig. 4.3a-b). The large and abundant

Zrn from Abu Rusheid have Hf contents that are much lower, with an average HfO_2 concentration of ~ 4 wt. %. The F contents are also lower, generally around ~ 0.5 wt. %. Raman spectroscopy and CL imaging of several grains show a range in degree of metamictization (Fig. 4.3c-d; Supp. Fig. 4.5), from crystalline to heavily metamict. The small zircon crystals from Abu Rusheid have Raman spectra akin to those from Abu Dabbab, as both are heavily metamict. However, some regions within the large zircon grains from Abu Rusheid show a high degree of crystallinity (Geisler et al., 2001). These are potentially suitable for dating by *in situ* methods, but very careful targeting of analytical spots would be required, and they may be post-magmatic in origin and age.

Fluorite Flr is almost perfectly stoichiometric at Abu Rusheid, with average composition $\text{Ca}_{1.0}\text{F}_{2.0}$, although a few analyses have substantial yttrium or REE concentrations (up to 6 and 12 wt. %, respectively). Flr from Abu Dabbab has very little REE and no Y.

Columbite-Tantalite Group Both localities have accessory columbite, ranging from more Fe- and Nb- rich at Abu Rusheid to more Mn- and Ta- rich at Abu Dabbab (Fig. 7b). Only Abu Dabbab has tantalite-(Mn) and wodginite. In a few examples, samples from Abu Dabbab contain zoned crystals with cores of columbite and rims of tantalite (Fig. 2e).

Cassiterite Chemically, cassiterite from Abu Rusheid is very nearly pure SnO_2 , but samples from Abu Dabbab show between 2 and 8 wt. % Ta_2O_5 .

Additional phases. Thorite and other U-bearing phases have average F contents of ~2 wt. % and oxide totals around 87%, suggesting hydration. The low concentrations of Pb within many of these grains, despite their extreme U and Th content and Neoproterozoic ages, suggest Pb loss from the minerals. Radiation damage forms halos around most of these grains, which often have holes or low-temperature oxide precipitates (e.g., Fig 3a). At Abu Dabbab, none of the monazite grains observed in the current study were pristine or suitable for dating (Zi et al., 2024); the lead concentrations of all grains were below EPMA detection limits (<0.05 wt. %) and most grains had an irregular, patchy texture (Fig. 4.2c).

Abu Rusheid features two thorium phases with chemistries previously undescribed: an Y-bearing thorite and a fluorinated member of the rhabdophane group, similar to brockite or grayite. Due to the high degree of radiation damage, neither of these phases were sufficiently crystalline to determine a crystal structure or define a new mineral species. Attempts to identify a crystal structure by electron backscatter diffraction revealed that the fluorinated rhabdophane is extremely beam sensitive (Supp. Fig. 6). The yttrian thorite has an approximate composition of $\text{Th}_{1.6}\text{U}_{0.8}\text{Y}_{0.7}\text{Si}_{2.2}\text{O}_7\text{F}_1(\text{OH})_5$. The rhabdophane varies from calcium-rich, $(\text{Th}_{0.7}\text{Ca}_{0.6}\text{Ce}_{0.1})(\text{PO}_4)\text{F}_{1.5}\cdot\text{H}_2\text{O}$, to more cerium-rich, $(\text{Th}_{0.7}\text{Ca}_{0.1}\text{Ce}_{0.4})(\text{PO}_4)\text{F}_{1.5}\cdot\text{H}_2\text{O}$, where Ce includes lesser amounts of La, Pr, and Nd. Both varieties are

dominantly phosphates, but show minor sulfate substitution akin to that in tristamite. A few points were very lead-rich and no points analyzed were significantly uranic. The detailed chemistry of both phases is provided in Supp. Table 3.14.

Discussion

Trace element behavior

Samples from both localities are enriched in most trace elements when normalized to primitive mantle values (McDonough and Sun, 1995), with absolute depletions only in Sr, P, Eu, and Ti (Fig. 4.6a). Abu Dabbab also is depleted in Ba and Y. These plutons show profound enrichments ($>100\times$ primitive mantle) in Rb, Th, U, Nb, Ta, Hf, and (at Abu Rusheid) Zr. Note that the normalized spider diagrams for these granites must span over six orders of magnitude to adequately display all data points. While the overall patterns for the two plutons are similar in the spider diagrams, there are a few notable differences. In samples from Abu Dabbab, there are steep differences between the geochemically “twinned” element pairs Nb-Ta and Zr-Hf, which are more muted in samples from Abu Rusheid. This results in characteristic elemental ratios for each pluton, namely very low Nb/Ta and Zr/Hf ratios at Abu Dabbab and higher ratios at Abu Rusheid (Supp. Table 2; Irber, 1999). Another difference in the plutons is the sharp valley in Y present at Abu Dabbab and absent at Abu Rusheid. As a result, Y/Ho, another elemental ratio whose behavior can be used to distinguish between charge-and-radius-controlled (CHARAC) and other petrologic processes, is also low in samples from Abu Dabbab. While the shape of

the spider plots is dependent on the ordering of the elements, the ratios between elements are independent of plotting choices.

On a chondrite-normalized plot of the lanthanides (Fig. 6b; McDonough and Sun, 1995), almost all the granitoids exhibit a slight to moderate enrichment in heavy rare-earth elements (HREE) relative to light rare-earth elements (LREE), with $(La/Yb)_n$ values generally less than 0.60 (the subscript n indicates chondrite-normalized concentration). Samples also show strong to extreme depletion in Eu at Abu Rusheid, with an average Eu/Eu^* value ($Eu/Eu^* = [Eu]_n / ([Sm]_n * [Gd]_n)^{0.5}$) of 0.14, excluding a group of 6 samples whose Eu analyses were below detection limit ($Eu/Eu^* \leq 0.004$). These strongly negative Eu anomalies suggest significant plagioclase fractionation.

Eu/Eu^* values for samples from Abu Dabbab occur over a wide range, with some samples showing slight to moderate Eu anomalies across a factor of two in either direction from unity ($Eu/Eu^* = 0.57 - 2.08$) and others with strong but unquantified negative Eu anomalies ($Eu/Eu^* \leq 0.004$) because Eu concentrations are below detection limits. Other than the depth of the Eu anomaly, there is no difference in the REE patterns between these two groups of Abu Dabbab samples. The slight positive anomaly would indicate that Abu Dabbab is a primary melt that did not experience significant fractionation, while the slight negative anomaly would suggest some fractionation of plagioclase. However, half of the granite samples analyzed had Eu concentrations below detection limits ($[Eu] < 0.11 \mu g/g$) despite overlapping ranges

of Sm and Gd concentrations with the Eu-bearing samples, implying a significant fractionation in otherwise identical rocks. One interpretation of the coexistence of these Eu signatures might be that the whole pluton experienced extensive plagioclase fractionation, drawing Eu down to below detection limits, followed by refertilization of some samples by a REE-bearing fluid with small and variable Eu anomalies. However, such a fluid would need to bring in significant REEs to cover the signature of prior Eu fractionation and hence implies a correlation between Eu anomaly and Sm concentration; no such correlation is present. Another possibility is that the Eu in the Eu-bearing samples is carried in plagioclase, which might then be absent in the Eu-free samples; however, all samples are plagioclase-rich. In summary, no magmatic hypothesis is likely to be able to explain the Eu data from Abu Dabbab.

The REE tetrad effects (i.e., differences in normalized concentration between the middle pair and outer pair of each group of four consecutive REEs) of these two plutons result in similar “M-type” anomalies, more pronounced at Abu Dabbab than at Abu Rusheid. $T_{1,3}$ values ($T_1 = ([Ce]_n * [Pr]_n) / ([La]_n * [Nd]_n)$; $T_3 = ([Tb]_n * [Dy]_n) / ([Gd]_n * [Ho]_n)$; $T_{1,3} = (T_1 * T_3)^{0.5}$; Irber 1999) are greater than one, with averages of 1.99 at Abu Dabbab and 1.48 at Abu Rusheid. Notably, several samples from both locations yield tetrad effects greater than 2. The effects at both localities are strongest in the LREE and weakest in the HREE, with an average T_1 and T_3 of 1.61 and 1.19 at Abu Rusheid, and of 2.26 and 1.52 at Abu Dabbab, respectively. Although the ranges in total REE content for the two plutons overlap, the range for Abu Rusheid

is much larger and the average ΣREE is notably higher (146 $\mu\text{g/g}$ for Abu Rusheid vs. 32 $\mu\text{g/g}$ for Abu Dabbab).

Granite magma type and P, T, $f\text{O}_2$ conditions

The strongly peraluminous nature of both plutons is often associated with melting of metasedimentary sources, which is supported by mineralogy (e.g., garnet, two micas) similar to traditional “S-type” granites (Chappell and White, 1974). However, highly ferroan and alkalic whole-rock chemistry in peraluminous samples, combined with high concentrations of HFSEs and LILEs, led to the classical definition of “A-type” granites (Collins et al., 1982). A review by Frost and Frost (2010; references therein) concludes that the combination of ferroan and peraluminous chemistry requires that these rocks are either the result of partial melting of intermediate metaigneous crust at high pressures (>0.6 GPa) or at lower pressures with a significant degree of crustal assimilation. The latter hypothesis is more appropriate for both plutons in this study, as discussed below.

To constrain the temperature of magma formation, the zircon saturation temperature was calculated following the method of Boehnke et al. (2013; Khedr et al., 2023). The garnet-bearing and garnet-free leucogranite of Abu Rusheid yielded temperatures several hundred degrees lower than the pink and main-body granite samples (730-830 °C to 1040-1120 °C, respectively). The leucogranite of Abu Dabbab had saturation temperatures around 780 °C, similar to the leucogranite units at Abu Rusheid. These numbers should be treated as upper limit estimates of

temperature, as zircon likely saturated before the majority of the pluton began to crystallize. However, they are still useful, as they suggest disparate conditions of formation between the units at Abu Rusheid. Neither Ti-in-zircon nor Ti-in-quartz thermometry were attempted due to the heterogeneous and inclusion-rich nature of these phases.

Unfortunately, pressure is more difficult to constrain, as these plutons are devoid of amphiboles or pyroxenes, which are considered the most reliable barometers. Attempts to apply the barometer of Yang (2017; Khedr et al., 2023) to samples resulted in an inappropriate range of pressures, from <0 to 2400 MPa, with averages of 330 and 560 MPa at Abu Rusheid and Abu Dabbab respectively. The garnets present at Abu Rusheid are Mn-rich and Mg-poor, providing constraints on pressure (≤ 300 MPa; Green, 1977) and temperature (≤ 650 °C; Speer and Becker, 1992) for garnet growth.

Two methods were applied to estimate the fO_2 of the magmas at these plutons. Select zircon from Abu Rusheid was analyzed by X-ray absorption near-edge structure (XANES), using uranium oxidation state to calculate oxygen fugacity (Houchin et al., 2024). This yielded results of $\Delta FMQ = 1 \pm 0.8$ (that is, about 1 log unit more oxidizing than the quartz-fayalite-magnetite buffer). Additionally, thirteen zinnwaldite-bearing samples and one fluorophlogopite-bearing sample from Abu Rusheid were approached using the methods of Bucholz et al. (2018) with success. In two samples, the calculated zircon saturation temperatures are higher than the

calibration range of Bucholz et al. (2018) in two samples. In eight samples the whole-rock MgO content is below the limit of detection. In the three remaining samples, the predicted fugacity of the phlogopite-bearing assemblage is several orders of magnitude different than that of the zinnwaldite-bearing assemblage, despite being the same lithology.

In summary, although the temperature of zircon saturation can be estimated for the two plutons, it is not representative of the formation conditions of either magma, and neither pressure nor fugacity calculations based on whole-rock and/or mineral chemistry yielded satisfactory estimations of magma conditions. Therefore, it is necessary to look elsewhere to evaluate the complex histories of these two plutons.

Magmatic versus post-magmatic processes

The whole-rock data indicate these both of the studied plutons have complex petrologic histories, including magmatic stages, high-temperature fluid alteration (e.g., metasomatism), and low-temperature alteration (e.g., weathering); potentially there were multiple episodes of the latter two processes. The following discussion will demonstrate that the high-temperature fluid alteration is best recorded in these rocks, and the most important process for understanding their mineralization.

Magmatic processes can generally be identified in major and trace element diagrams, plotting various elements against SiO₂ as a proxy for differentiation or fractionation. However, both locations lack significant trends in nearly all conventional Harker

diagrams. Data that do not form coherent trends in variation diagrams are not easily explained by traditional magmatic differentiation models such as fractional or batch crystallization. Examples of unsatisfactory rhyoliteMELTS (Ghiorso & Gualda 2015) calculations, as well as melt-crystal mixing (after Abuamarah et al. 2023), are provided in the supplement.

It is evident in hand-sample and thin-section that these rocks are altered and it is possible that none of the sampled rocks preserves magmatic mineral or bulk compositions. This interpretation is supported by the near end-member albite and potassium feldspar present at both locations (at magmatic conditions, we expect more extensive solid solution in the feldspars); secondary fluorite; fracture-filling oxides; and low Pb content of U-rich phases indicating lead loss. Many major and minor phases show precipitation and dissolution textures along their boundaries, which are accompanied by interstitial hydrous Fe and Mn oxides, with the latter being more dominant at Abu Dabbab (Supp. Table 3). There are also samples that can be termed greisens and veins, with non-magmatic modal compositions, and some samples from Abu Rusheid are so strongly foliated they have been described as gneisses (e.g., Ali et al., 2011; Raslan 2005).

Loss on ignition (LOI), the chemical index of alteration (CIA), and the weathering index (WI) are all geochemical tools used for constraining low-temperature alteration (González-Menéndez et al., 2022; Gong, et al., 2013). However, LOI of these rocks does not serve as a useful proxy, as almost all samples yielded values between 0.5

and 1.5%. Applying CIA and WI to these samples suggests that the rocks that are least weathered include those with abundant secondary phases or gneissose textures, which logically should be more altered (Supp. Table 2). Similarly, the core samples collected from depth cannot be resolved from the surficial samples with these proxies. Despite the prevalence of low-temperature phases, these results indicate that surficial weathering and supergene enrichment are not the dominant secondary processes for either pluton, leaving hydrothermal (hypogene) processes. It should be noted that the most recent pulse of hydrothermal activity occurred around 17.9 Ma, accompanying the opening of the Red Sea Rift (Geisler et al., 2003). This fluid is likely to blame for the recent leaching of radiogenic lead from U- and Th-bearing phases, a process aided by the extensive radiation damage observed in these rocks. This hydrothermal activity is probably the cause of some irregular mineral textures, including the cauliflower texture of thorite and the patchy appearance of albite. It is likely that this event did not feature a fluorinated fluid, and involved circulation through near-surface tensile fractures of a low temperature aqueous solution (<200°C, Geisler et al., 2003).

Fluid inclusions were observed in thin section. At Abu Dabbab, fluid inclusions show evidence of multiple episodes of trapping. The larger inclusions in quartz show inverted crystal shapes (Supp. Fig. 4.1d) and occasionally appear to show vapor bubbles, characteristic of being primary fluid inclusions (i.e., syn-magmatic). Additionally, inclusions in feldspar show alignment with crystallographic axes

(Supp. Fig. 4.1e), another signifier of primary fluid inclusions. Both localities have secondary fluid inclusions, which could be identified as very small ($<1\ \mu\text{m}$) bubbles occurring along planes representing healed fractures (e.g., Wilkins and Barkas, 1978; Supp. Fig. 4.1f). In some cases these cracks extend across multiple grains, a signature of subsolidus brittle processes. Many large grains (e.g., plagioclase) are fractured with either voids or amorphous phases in the cracks (Fig. 4.6b, c), implying at least some processes occurred when the rocks were cool enough to have a brittle response. Multiple iterations of growth and zonation observed in zircon and columbite-tantalite grains, on the other hand, suggest high-temperature post-magmatic mobilization of HFSEs. Evidently, the history of these rocks is complex. The fluid inclusions of Abu Dabbab were studied in detail by Zoheir et al. (2020); they are low in Cl and high in CO_2 (F was not determined).

Metasomatic and high-temperature alteration at Abu Dabbab

Abu Dabbab shows evidence for a fluid-rich magmatic system, followed immediately by an episode of autometasomatism, then very little activity until the hydrothermal activity around 17.9 Ma (Geisler et al., 2003).

The major hydrothermal event featured the precipitation of cassiterite, scheelite, and oxides, indicating the fluids were laden with metals. The presence of fluorite and muscovite around the edge of zinnwaldite grains suggests the mobilization of fluorine out of magmatic mica during this high-temperature event. Previous work to constrain the magmatic-hydrothermal transition of the Abu Dabbab system used magmatic

monazite and hydrothermal cassiterite to date the magmatism to 644.7 ± 2.3 Ma and the hydrothermal activity to 644.2 ± 2.3 Ma (Lehmann et al., 2020). While this is consistent with the expectation that the hydrothermal activity is younger than the magmatism, the events are not resolvable in age with this method. If the granite itself was the source of fluids (i.e., autometasomatism), a rapid shift from magmatic to hydrothermal crystal growth would be expected (Bau, 1996; Sami et al., 2022). It may be that the rapid temporal evolution inferred by Lehmann et al. (2020) is due to the resetting of lead (even in magmatic phases) during the hydrothermal event. Given the limited presence of fluorite and its localization around zinnwaldite, this event most likely records a redistribution of fluorine, rather than its introduction into the system. This event was likely the event in which the plagioclase at Abu Dabbab underwent albitization, making plagioclase the probable source for the Ca for fluorite.

There is further evidence to suggest a late-magmatic or metasomatic event that caused the growth of tantalite-(Mn) rims around grains of columbite-(Mn). Diao et al. (2024) concluded, in similar rocks, that the gradual change in composition from more Fe- and Nb-rich to more Mn- and Ta-rich in columbite group minerals is consistent with a magmatic origin. However, the abrupt change around the rims observed in this case (Fig. 4.6e) instead marks interaction between primary magmatic phases and a “hydrosilicate” fluid. Such fluids, with roughly equimolar contents of H_2O and SiO_2 , would have transitional properties between aqueous fluids and silicate

melts, able to complex both Nb and Ta but with a different Nb/Ta uptake ratio compared to a less hydrous silicate melt. The profound fractionations observed between geochemical twins (Zr & Hf, Y & Ho, Nb & Ta) at Abu Dabbab are more likely the result of a silicic aqueous fluid, rather than a silicate melt with fluid-like behavior (Bau, 1996; Ballouard et al., 2016). This is further supported by the fluid inclusions described by Zoheir et al. (2020). The presence of greisen around the edges of the pluton, as well as miarolitic cavities containing large crystals of lithian micas, topaz, and tourmaline, support a volatile-rich, late- or post-magmatic silicic fluid sourced from the pluton itself. As this event evidently mobilized REE+Y sufficiently to fractionate Y from Ho, it is not unreasonable to infer that the same event mobilized Eu and led to the below-detection limit Eu concentrations in some granite samples.

The actual magmatic evolution of Abu Dabbab can still be interpreted from the igneous textures of the rocks and the chemistry of selected minerals. The presence of nearly euhedral snowball quartz with albite inclusions suggests rapid growth as a result of undercooling (Zhang et al., in press). If the inference of a very short time-interval between magmatic and hydrothermal activity inferred by Lehmann et al. (2020) is correct, this would be consistent with rapid cooling below the liquidus during the magmatic stage of this small, high-level intrusion. The magma would have been fluorinated, evidenced by the elevated fluorine contents of nominally fluorine-free minerals, such as thorite, and the presence of primary fluorinated micas, bastnäsite-(Ce), and F-bearing microlite. Fluorination would have aided the transport

of Nb, Ta, and other HFSEs, as well as the mobilization of these elements into the surrounding rocks (Aseri et al., 2015; Supp. Fig. 4.7f).

The intrusion of Abu Dabbab occurred during a period of quiescence between major pulses of magmatism in the Eastern Desert (Lundmark et al., 2012), and there are no other plutons within 20 km of it to provide further context (Fig. 4.1). The Najd Shear zone was active at this time, and while there may be affiliated faults in the area around Abu Dabbab (Hamimi et al., 2019), there is no evidence for substantial activity (i.e., no shearing of the granite). There may be a mechanical decoupling below the pluton, between layers of basement succession, a structural weakness that could explain the location of the body in the middle of undifferentiated island arc and metamorphic rocks.

In conclusion, there is mineralogical and chemical evidence that the rare-metal fluids that generated the Ta (and Sn) deposit were self-sourced. The pluton crystallized rapidly, then continued to simmer in its own metasomatic fluids, which would have been silicic aqueous fluids capable of creating unusual Nb/Ta, Zr/Hf, and Y/Ho ratios. The history of Abu Dabbab is summarized in [Fig. 4.8a](#).

Repeated high-temperature events at Abu Rusheid

As with Abu Dabbab, there is regional evidence to support a large-scale hydrothermal event at Abu Rusheid in the Miocene (Geisler et al., 2003), featuring the mobilization of radiogenic Pb from U- and Th- bearing minerals and accompanied by local sulfate

deposition, primarily as jarosite, anglesite, baryte, and gypsum, as well as hydrous iron oxides. There is also evidence of reprecipitation of many pyrochlore group minerals during this time, filling in the radiation damage 'halos' of other grains of pyrochlore, samarskite, etc. However, unlike Abu Dabbab, Abu Rusheid shows evidence for many episodes of alteration before this recent activity.

Lundmark et al. (2012) studied a series of plutons along the Nugrus thrust in the area around Abu Rusheid and determined that a significant mineralization event occurred around 608 Ma, fluxing the system with Nb, Ta, and U. The authors interpreted this to be one hydrothermal event caused by a nearby granitic intrusion, but the combination of an active fault system, extensive metamorphism, and multiple pulses of local magmatism may have resulted in numerous events (Dawood et al., 2010). During one or more of these events, the Abu Rusheid granite underwent Na- and K-metasomatism and, locally, silicification (e.g., Skt 29). Unlike Abu Dabbab, very few of the mica grains from Abu Rusheid show discrete rims. Due to the large number of sulfides in the rock, there is evidence to support a post-magmatic sulfur mobilization event involving the growth of minerals like galena and pyrite, both on existing phases and in vesicles. Some of these secondary sulfides were altered to sulfates during the youngest alteration event. Similarly, in the area around radioactive phases, iron oxides also grew during these events, as some show minor radiation damage which was then filled by more recent iron oxides. There are also many phases that show dissolution-precipitation textures (Fig. 4.6f), supporting the involvement of metal-

bearing fluids. The mobilization of Nb and Ta, as well as the fracture-lining fluorite, suggests that the fluids in at least one of these events were fluorinated.

The magmatic history of Abu Rusheid is multifaceted, as there is chemical and textural evidence that the different lithologies experienced different crystallization conditions. The garnet-bearing granite (GBG) whole rock chemistry cannot be created from the garnet-free, main body granite (MBG) simply by adding or subtracting garnet. The trace element patterns are similar, with the primary difference being in the relative concentration of metals, and a slight enrichment of HREE over LREE in the MBG, indicating similar sources. However, the sharp contact between the GBG and MBG units suggests discrete magma pulses. The garnets show no compositional zoning, and there is no discernable chemical difference between the mineral inclusions and their external counterparts (i.e., muscovite hosted by garnet is identical to muscovite elsewhere in the rock). As the garnet is uniformly Mn-rich and Mg-poor, the granite is likely to have formed at low pressure (<300 MPa; Green, 1977) and low temperature (<650 °C; Speer and Becker, 1992). Garnet-free leucogranites from Abu Rusheid share many chemical features with the GBG and are likely samples sourced from the same body without garnets visible in thin section.

The rare-metal MBG has evidence for multiple growth periods, interpreted from the complex textures of its zircon. The interiors of these grains are filled with inclusions, are unreactive in CL, have no evidence of compositional zoning, and have a metamict Raman signal, accompanied by low totals. From some imaging, it appears this

domain is euhedral in many samples. Some grains show evidence of epitaxial growth around this inner zone. The rims, on the other hand, are inclusion poor, CL bright, and yield Raman peaks with a crystalline signal. The only chemical difference between the inner and rim domains is a decrease in U and Th in the rim. It is unlikely that the cores are inherited from older rocks, as inherited zircons are infrequent in intrusive rocks from the Nubian Shield (Johnson 2021). Instead, there was a period of rapid crystallization of many Th and U phases (e.g., thorite) in the middle of zircon growth, supported by the horizon of thorite observed in some grains (Fig. 4.6d). In many samples from this facies, there is a gradational evolution of some columbite group minerals from more Fe-rich to Mn-rich, evidence for magmatic evolution (Diao et al., 2024), and the inclusion of columbite in zircon, of monazite in zircon, of zircon in columbite, etc., supports the co-magmatic nature of most of the rare-metal phases. The mineralogy of the MBG makes thermobarometry estimates challenging. Attempts to apply the 2-feldspar thermometer of Brown and Parsons (1984) on the least altered plagioclase yields a minimum temperature of about 650 °C. An application of the Seydoux-Guillaume et al. (2002) thermometer to the thorium content of monazite gives a minimum temperature of ~550 °C at 200 MPa. These are both consistent with experimental work on the effects of fluorine on the granite minimum, which can depress the liquidus to <630 °C at 100 MPa (Manning 1981). These temperatures represent estimates of final crystallization and are far below the zircon saturation temperature calculated in the discussion above (~1100 °C). Late

magmatic aplite veins, geochemically more similar to the GBG, cut through the pluton after it had mostly solidified.

Abu Rusheid lies on the Nugrus Fault, adjacent to the Zabara orthogneiss and Hangaliya granite (Mubarak et al. 2026). The magmatic ages of its neighbors are 633 and 629 Ma (Lundmark et al., 2012), perfectly overlapping with Abu Rusheid, dated to 629 Ma (Ali et al., 2011). This large-scale event, the third pulse of Lundmark et al. (2012), is observed in other locations through the Eastern Desert, including the deformation of the lower Meatiq gneiss. The granites of this time are interpreted to be transitional in chemistry, from a synorogenic setting to a within-plate environment. Due to the activity in the Najd Shear belt, Abu Rusheid (unlike Abu Dabbab) was a part of a broad, geochemically open system throughout the Ediacaran.

In conclusion, multiple magmatic and hydrothermal pulses are recorded at Abu Rusheid. This, combined with its placement on a highly active fault, indicate that the pluton has undergone many alteration events. There is no evidence to suggest that the hydrothermal activity here was self-sourced, and the pluton should be approached as an open system. The history of Abu Rusheid is summarized in [Fig. 4.8b](#).

Use of fluorine as a mineral prospectivity indicator

Considering only whole-rock chemistry, F concentration does not show a simple correlation with Nb or Ta concentration within either pluton or between plutons. However, there are some notable predictors. At Abu Rusheid, among the one hundred

samples studied, all those with $>5000 \mu\text{g/g}$ F also have at least $50 \mu\text{g/g}$ Ta and $400 \mu\text{g/g}$ Nb. At Abu Dabbab, among 23 granite samples, only two have $>4000 \mu\text{g/g}$ F and while one of these is extremely mineralized, the most F-rich sample from this locality has Ta and Nb concentrations typical of the whole pluton. However, almost all samples have concentrations in the range of $1000\text{--}4000 \mu\text{g/g}$, and even the least fluorinated sample is still enriched compared to average granite ($\sim 600 \mu\text{g/g}$; Wedepohl 1995; Gao et al., 1998).

At the mineral chemistry level, high F content in zinnwaldite may be an indicator of elevated HFSE concentration ([Supp. Fig. 4.7](#)). All the Abu Rusheid granite samples with $\geq 80 \mu\text{g/g}$ Ta and $\geq 500 \mu\text{g/g}$ Nb also contain zinnwaldite with at least 0.8 atoms of F per 11 O formula unit (apfu). Conversely, 90% of samples from Abu Rusheid containing zinnwaldite with ≥ 0.8 apfu F have $\geq 80 \mu\text{g/g}$ Ta and $\geq 500 \mu\text{g/g}$ Nb. However, Abu Dabbab samples contain F-bearing zinnwaldite that is uniformly lower in fluorine (<0.5 apfu), yet the whole-rock chemistry is more enriched in Ta than the Abu Rusheid samples.

Just as thermodynamically-informed models of fluorine-bearing magmatic systems are lacking, models of fluorine-bearing hydrothermal systems are in their infancy. More work is necessary to parse the episodes of mineralization, and to determine the sources and compositions of late- or post-magmatic fluids. As plutons, Abu Rusheid and Abu Dabbab make interesting case studies as open and almost-closed systems, respectively.

Source of fluorine and rare-metal magmas

The question remains as to the source of fluorine and the metals present in these plutons. Anorogenic and post-magmatic intrusions pose a puzzle generally, as they nominally intrude when there is no obvious cause of melt production. In the ANS, delamination of the lower lithosphere is invoked during the post-orogenic environment, as ascending hot mantle would melt and heat the lower crust (e.g., Avigad & Gvirtzman, 2009). Fluorine can be derived from the heating of biotite and /or amphibole in the lower crust, and amphibole is one of the few minerals that is capable of fractionating Ta from Nb (Ionov & Hofmann, 1995; Li et al., 2017). Much of the crust that made up the young ANS in the Neoproterozoic was arc-related rocks, and it is possible that small domains of amphibole-rich material underwent repeated crystallization and melting during both collision and delamination, concentrating Ta and F, until the last melt extraction event that resulted in Abu Dabbab. However, the lack of an amphibole-like REE pattern precludes a pocket of amphibole from being the primary source of the melt (Ionov & Hofmann, 1995).

Arcs and post-collisional magmatism are common tectonic environments on Earth, but metal deposits like those at Abu Dabbab and Abu Rusheid are rare. However, the ANS is recognized for having a diverse array of economic deposits, from Cu porphyrys to banded iron formations to epithermal gold deposits to dozens of rare-metal plutons (Botros 2021). There are still many questions about the geologic

context of this enriched terrain, but it is likely that the sources of these two plutons are closely related to the broader tectonics of the region.

Conclusions

The rare-metal granites from Abu Rusheid and Abu Dabbab share A-type character; both are strongly peraluminous and enriched in rare metals relative to the primitive mantle. Both localities show negative Eu anomalies and enrichments in HREE relative to LREE. However, these two plutons are chemically and mineralogically distinct. Abu Rusheid samples generally contain more rare-earth elements and rare metals than those from Abu Dabbab, bearing both LREE and HREE phosphates. However, Abu Dabbab is notably more enriched specifically in Ta and Mo. Abu Rusheid also bears more fluorinated mineral phases in higher abundances. The high content of fluorine in these magmas supports the need for a thermodynamic magmatic model that includes fluorine. However, the extensive hydrothermal alteration present at both localities suggests these plutons will not be useful in the calibration of such a model. Instead, these two bodies serve as examples of the evolution of critical metals in granite in two contrasting situations: a case of a pluton connected to a large, active hydrothermal system (Abu Rusheid) and a case of a pluton isolated from external metasomatic influence (Abu Dabbab).

Data availability

All the data will be published with the manuscript.

Acknowledgments

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Figures

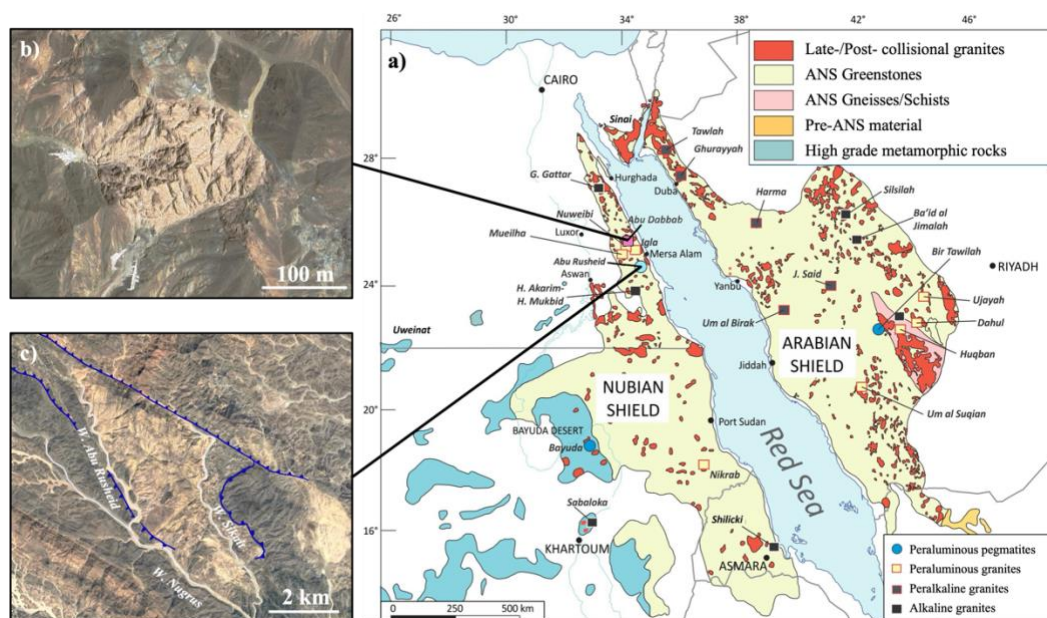
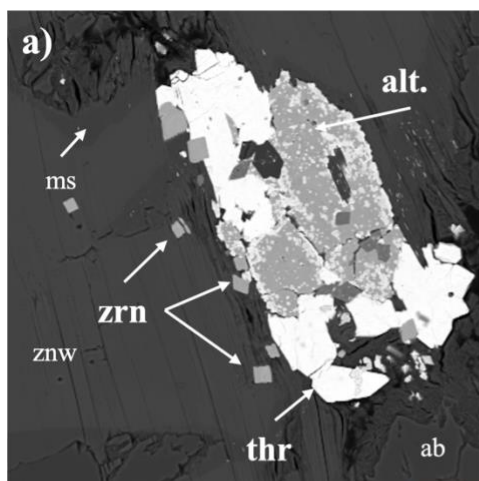
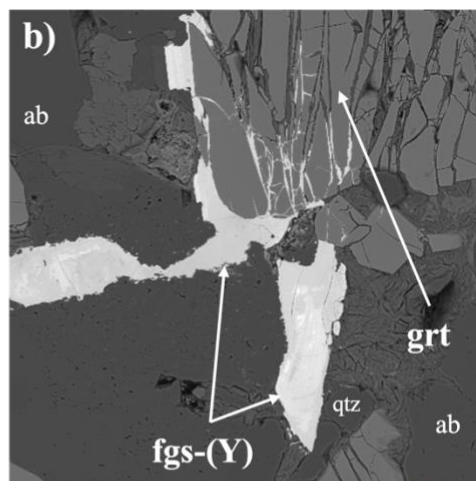


Figure 4.1 – Geography and regional geologic setting of the study areas

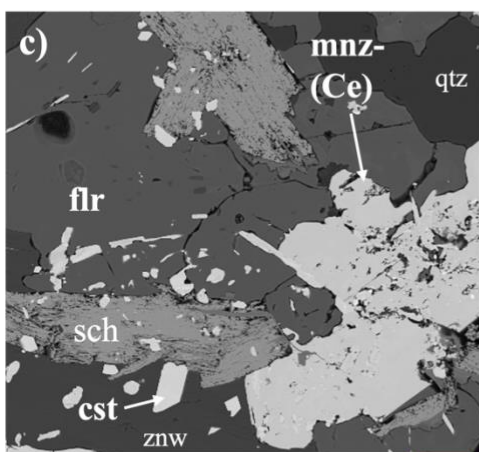
a) Regional setting of the Abu Rusheid and Abu Dabbab plutons in the Arabian-Nubian Shield (ANS). [b\)](#) Abu Dabbab and [c\)](#) Abu Rusheid satellite imagery (from Google Earth™) of the exposed granites. Tectonic features and washes (wadis) have been annotated where relevant. a) after Lehmann et al. (2020), c) after Ibrahim et al. (2000).



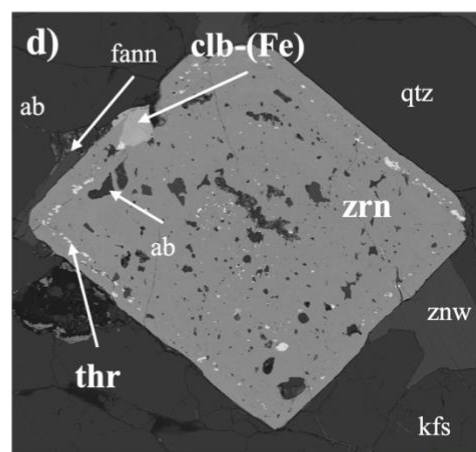
ADb2

20 μm 

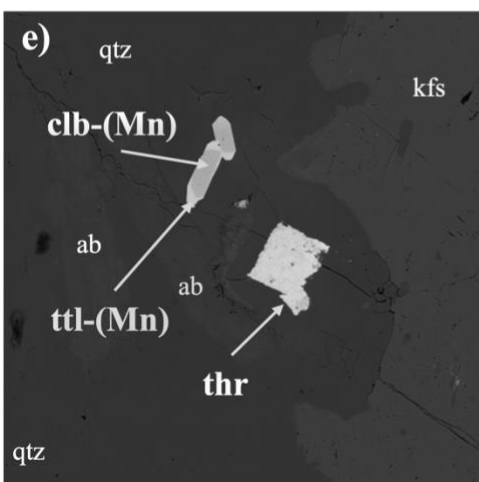
ARd34

30 μm 

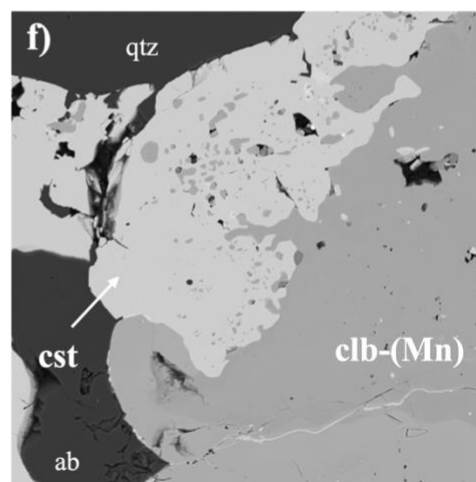
ADb15

30 μm 

ARd13

100 μm 

AD10

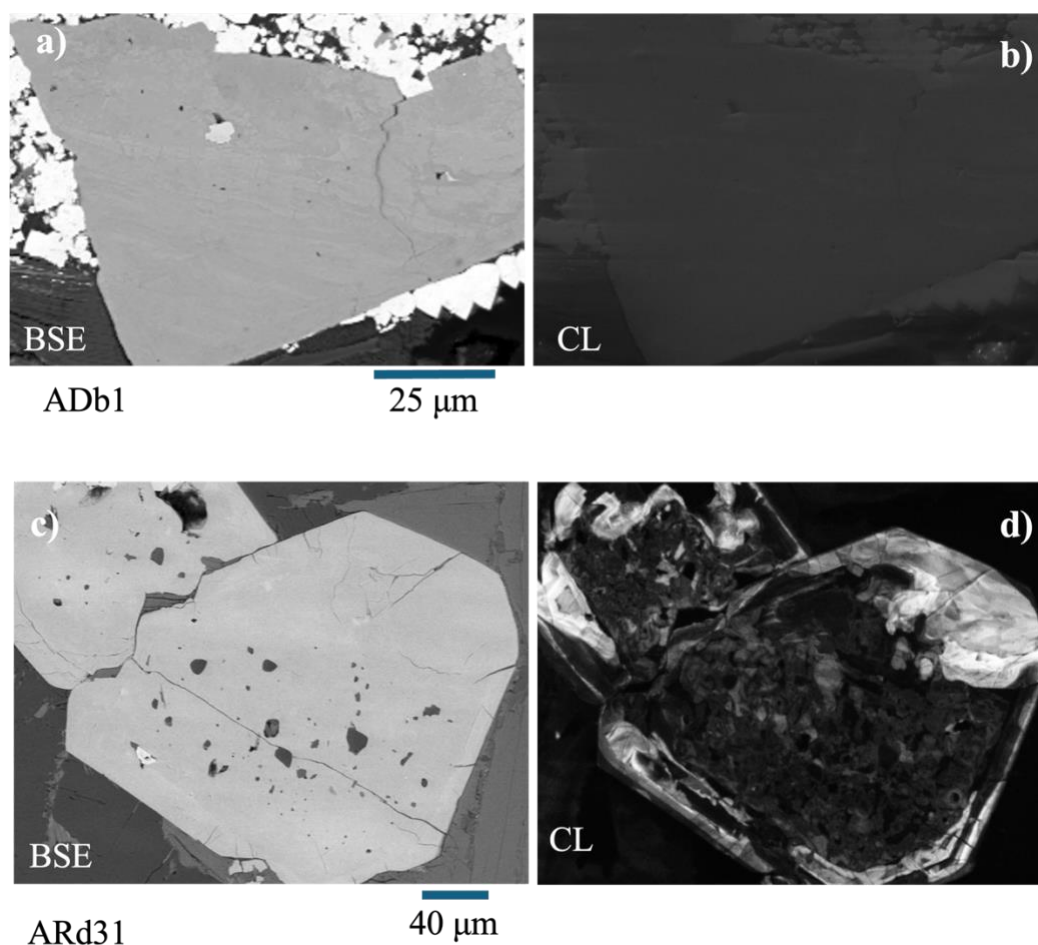
60 μm 

ARd16

20 μm

[Figure 4.2](#) – Back-scattered electron (BSE) microphotographs.

Images of various samples displaying the mineralogy and textures described in the text. a) euhedral grains of zircon with thorite, Abu Dabbab (A.D.); b) fractured garnet from Abu Rusheid (A.R.); c) rare-metal phases enclosed by feldspar and alteration phases, A.D.; d) large subhedral grain of zircon with inclusions of thorite, albite, columbite, and quartz, A.R.; e) columbite grains with tantalite rims, A.D.; f) embayed columbite and cassiterite, A.R. Abbreviations as follows: qtz – quartz, kfs – K-feldspar, ab – albite, znw – zinnwaldite, ms – muscovite, fann – fluoroannite, zrn – zircon, thr – thorite, grt – garnet, clb-(Fe) – columbite-(Fe), clb-(Mn) – columbite-(Mn), ttl-(Mn) – tantalite-(Mn), fgs-(Y) – fergusonite-(Y), mnz-(Ce) – monazite-(Ce), flr – fluorite, sch – scheelite, cst – cassiterite, alt. – hydrous alteration product.



[Figure 4.3](#) – Zircon BSE and CL images.

BSE and cathodoluminescence (CL) images of zircon from Abu Rusheid (A.R.) and Abu Dabbab (A.D.). a) BSE and b) CL images of a zircon grain from A. D. surrounded by ‘cauliflower’ thorite. No zoning or growth patterns are visible in CL. c) BSE and d) CL images of a subhedral grain of zircon from A.R. In CL, the rims are strongly visible as bright zones around a dark and jumbled interior.

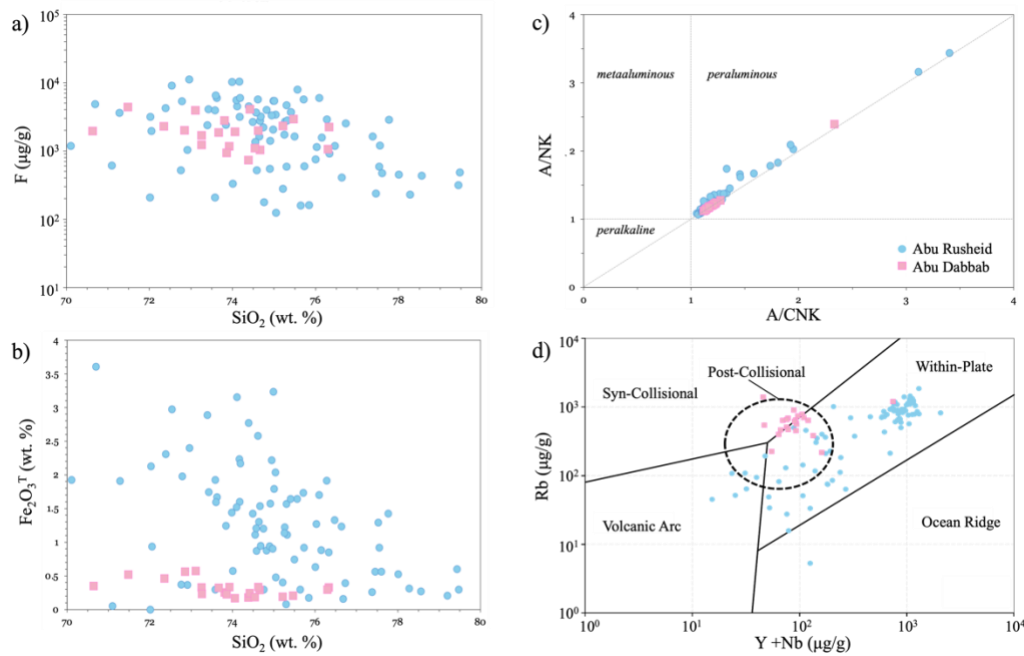
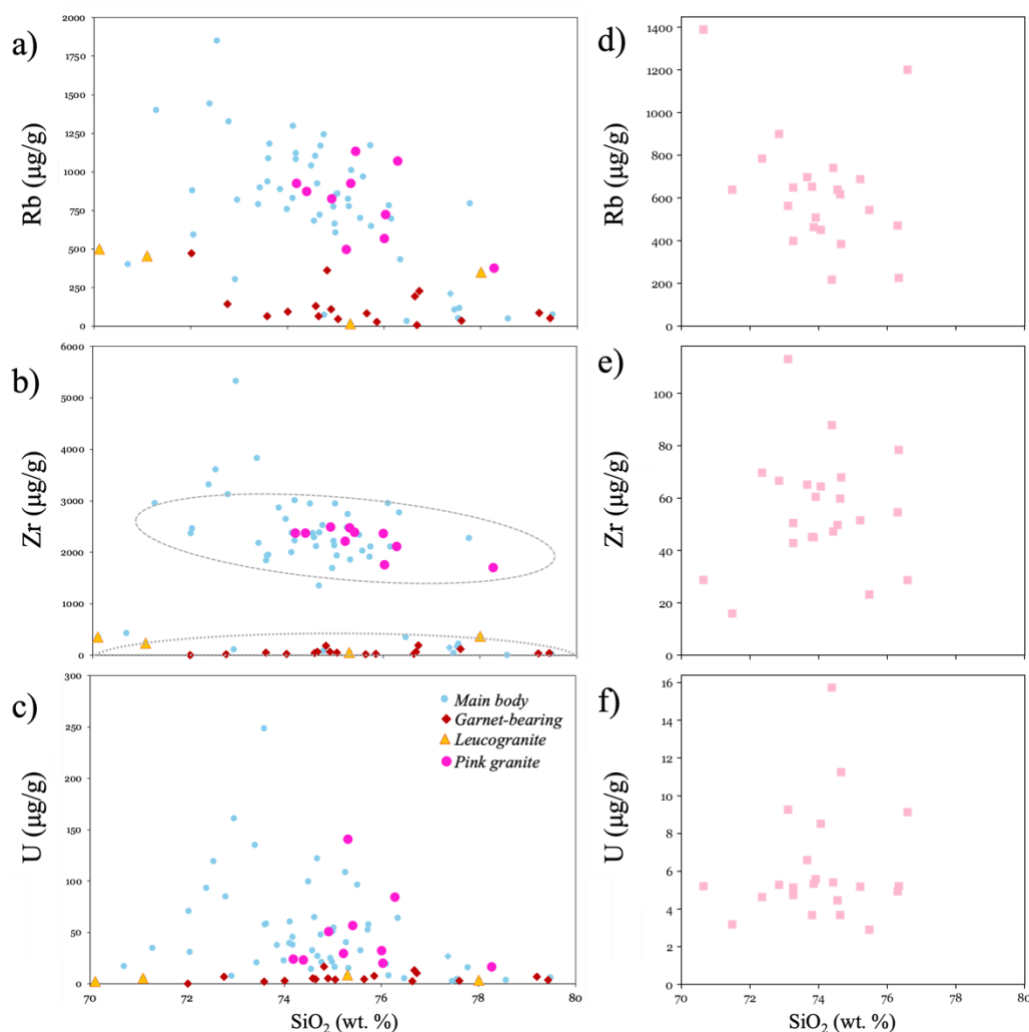


Figure 4.4 – Whole-rock geochemistry diagrams.

a) Harker diagram of SiO_2 against whole-rock F. This is a log-linear plot to best show the entire range of fluorine content. B) Harker diagram of SiO_2 against total iron as Fe_2O_3 . C) A/CNK ($[\text{Al}]/[\text{Ca}]+[\text{Na}]+[\text{K}]$) against A/NK ($[\text{Al}]/[\text{Na}]+[\text{K}]$) diagram indicating all samples are peraluminous. d) Rb versus Y+Nb discrimination diagram from Pearce et al. (1984). Samples from Abu Rusheid show a variety of apparent chemical affinities, primarily within-plate and post-collisional, while almost all samples from Abu Dabbab plot in the post-collisional field. Rocks identified in hand sample as country rocks or monomineralic lithologies, including veins and aplites, are not shown.



[Figure 4.5](#) – Trace element plots.

Harker diagrams for Abu Rusheid (left) and Abu Dabbab (right), displaying Rb (a, d), Zr (b, e), and U (c, f). Note that the y-axes differ between the plutons but the x-axes show the same range. In the plots of Abu Rusheid, the symbols indicate different textural facies. In elements with bimodal behavior, the garnet-bearing and leucogranite samples behave similarly, making up the low, flat trend emphasized, while pink granites and most of the main body granites show elevated values. These are emphasized by the dashed ellipses in (b).

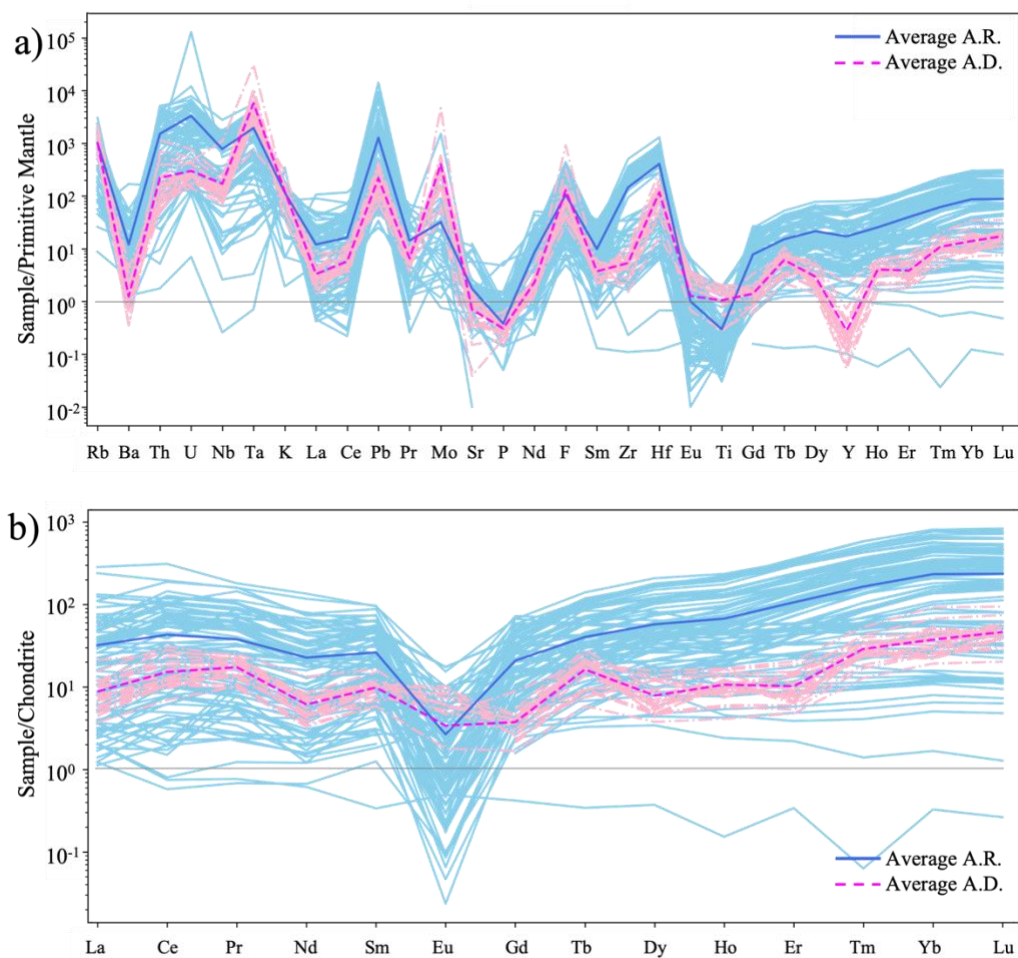


Figure 4.6 – Trace element spider diagrams.

Normalized multi-element whole-rock trace element pattern (spider diagrams) for the two plutons, Abu Rusheid (A.R.) and Abu Dabbab (A.D.). a) Trace elements relative to primitive mantle. b) Lanthanides relative to chondritic values. In both figures, all analyses are plotted along with the average for each pluton, shown as bold lines. A.D. lines are dashed and A.R. lines are solid. The flat grey line shows no enrichment. Normalization values are from McDonough and Sun (1995).

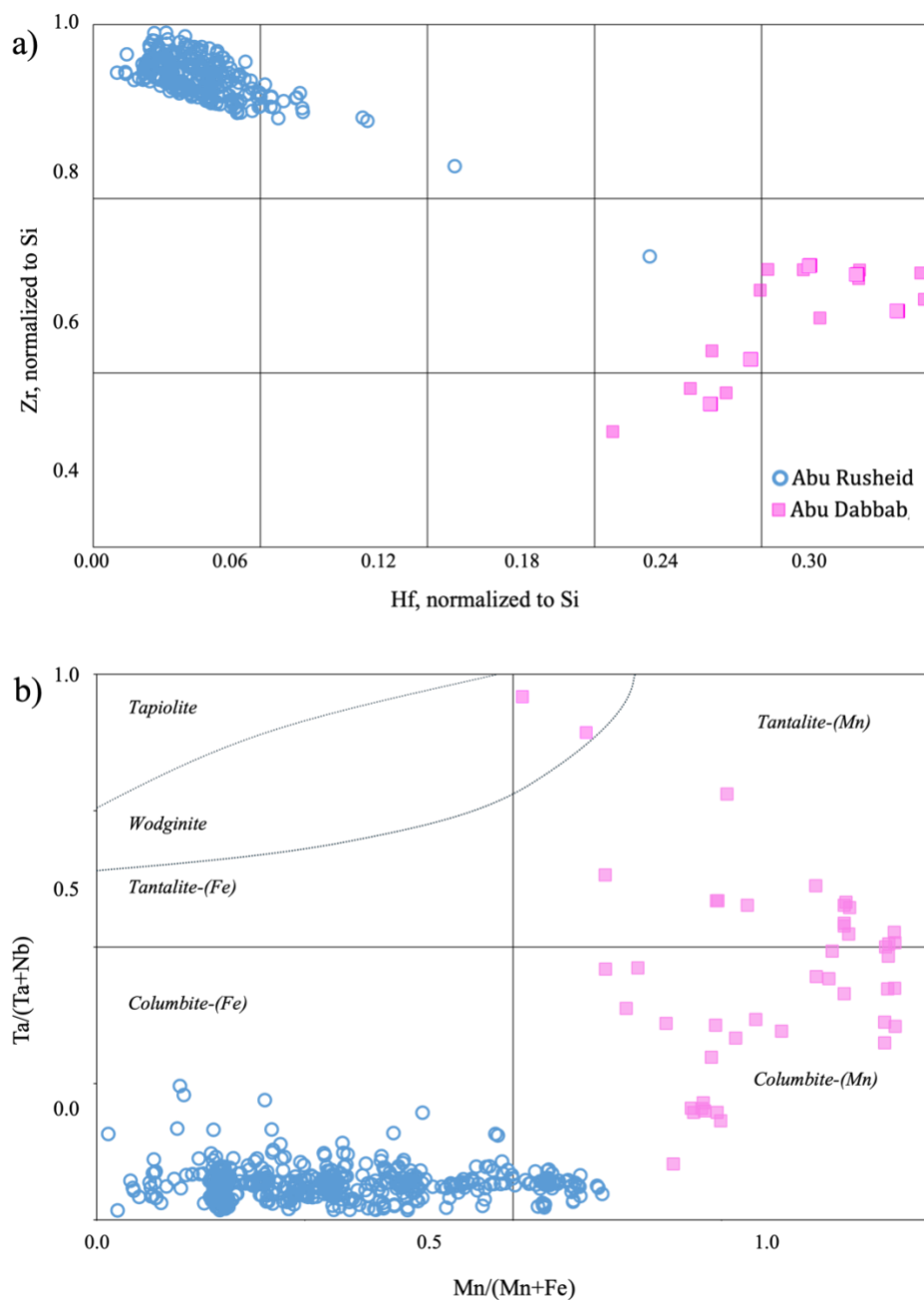


Figure 4.7 – Mineral chemistry plots from EPMA data.

a) Zr against Hf contents of zircon, normalized to Si. All samples from Abu Dabbab are low-total (<97 wt. %). B) Mineral chemistry of columbite-tantalite family, based

on $\text{Ta}/(\text{Ta}+\text{Nb})$ and $\text{Mn}/(\text{Mn}+\text{Fe})$ ratios. Both localities show a range of chemistry, but all phases from Abu Rusheid are Nb-rich while those from Abu Dabbab are Mn-rich.

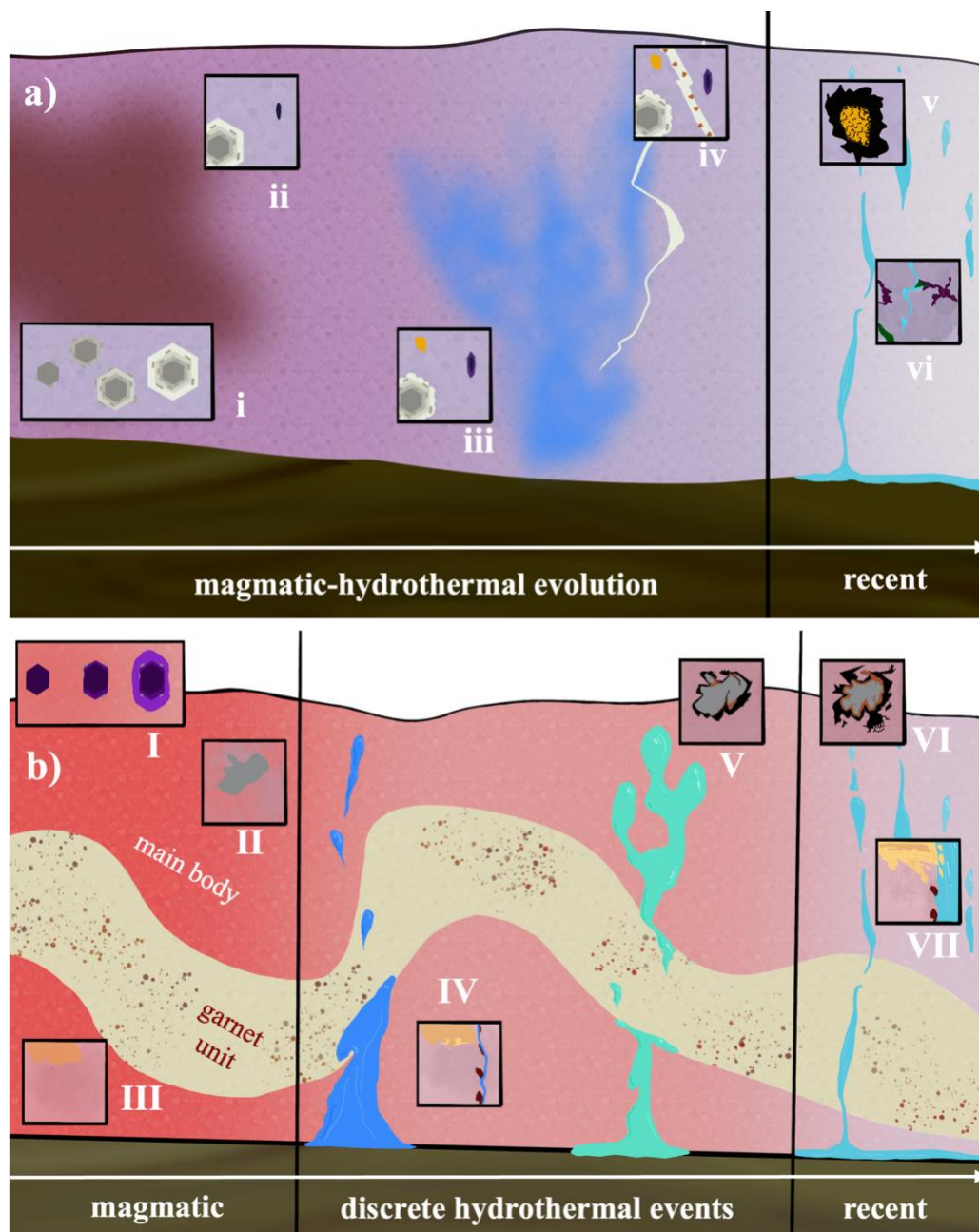


Figure 4.8 – Models for the evolution of the rare-metal granites.

Schematics of (a) Abu Dabbab and (b) Abu Rusheid plutons. At Abu Dabbab, the magmatic history saw the growth of many rare-metal phases and a rapid transition to hydrothermal behavior (i-iii). The end of the high-temperature system saw the intrusion of qtz veins, many of which bear cassiterite (iv). The pluton had little

significant activity until the Neogene, when warm fluids washed out radiation halos (v) and caused some dissolution and reprecipitation of Mn- and Fe-oxides (vi). At Abu Rusheid, the magma evolved rapidly, evidenced by the textures of zircons (I). Many U-rich phases (II) and major phases, including albite (III), also grew during the magmatic event in both the garnet-bearing leucogranite and the main body granite. There were several hydrothermal events throughout the Neoproterozoic, some of which introduced large amounts of fluorine to the system, precipitating fluorite (IV), in addition to albitization and secondary mineral precipitation. Over time, more generations of radiation damage occurred (V), filled with secondary phases during the recent hydrothermal event (VI). This event continued the overprinting of primary signatures in magmatic phases (VII).

Appendix IV.1: Methods

S1.1 Whole Rock analyses

Samples from Abu Rusheid include samples collected in 2020 with the following names (# samples):

- ARS (10), received at Caltech October 2020. All samples are granite.
- 1014 (9), received at Caltech October 2020. All samples are granite.
- Skt (22), received at Caltech November 2020. 13 samples are granite.
- NgR (24), received at Caltech November 2020. 22 samples are granite.
- Ard (35), received at Caltech November 2020. 32 samples are granite.

Samples from Abu Dabbab include samples collected in 2020 with the following names (# samples):

- AD (3), received at Caltech October 2020. All samples are granite.
- ADb (26), received at Caltech November 2020. 21 samples are granite.

Weathered rinds were removed from all samples before they were cut for thin section preparation and crushed for whole-rock analysis.

S1.2 XRF – Instrument and analytical details

Whole rock composition (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, MnO) was analyzed on fused beads using a Panalytical Zetium XRF. The analytical protocol is calibrated on the following USGS standards: AGV-1, AGV-2, BCR-1, BCR-2, BHVO-2, BIR-1, DNC-1, DTS-2, G-2, GSP-2, MAG-1, NKT-1, NOD-A-1, QLO-1, RGM-2, SBC-1, SCO-1, SDC-1, SGR-1b, STM-1, and W-2; as well as the following GSJ standards: JG-2, JGb-2, and JH-1. Detection limits are around 0.005 wt. % for all major elements. Exact limits are provided in Supplementary Table 1a. AGV-2, BCR-2, and RGM-2 were run alongside samples as unknowns for quality control. No drift correction was necessary. Conditions and settings are provided in Supplementary Table 1a.

F, Cl, and S were also analyzed on pressed pellets of unfired sample powder using the same Panalytical Zetium XRF, with a similar calibration protocol. The standards

used for this were: AGV-1, AGV-2, BCR-2, BHVO-2, BIR-1a, DNC-1, DTS-2b, G-2, GSP-2, JG-2, JGb-2, JH-1, MAG-1, NKT-1, NOD-A-1, NOD-P-1, QLO-1a, RGM-2, SCO-1, SDC-1, SSAR-1, STM-1, and W-2b. The analytical conditions and detection limits are presented in Supplementary Table 1a. GSP-2 and BCR-2 were run alongside samples for quality control.

Supplementary Table 4.1a – XRF conditions

Compound	Bead or pellet	Crystal	Collimator (μm)	Detector mode	kV	mA	Detection Limit (μg/g)
SiO ₂	Bead	PE	300	Flow	25	160	31
TiO ₂	Bead	PX10	300	Flow	40	100	11
Al ₂ O ₃	Bead	PE	300	Flow	25	160	16
Fe ₂ O ₃	Bead	LiF220	300	Scint	60	66	9
MgO	Bead	PX8	700	Flow	25	160	43
CaO	Bead	PX10	300	Flow	30	133	10
Na ₂ O	Bead	PX1	700	Flow	25	160	45
K ₂ O	Bead	PX10	300	Flow	25	160	6
P ₂ O ₅	Bead	Ge	300	Flow	25	160	8
MnO	Bead	PX10	300	Flow	60	66	3
F	Pellet	PX1	700	Flow	25	160	115
Cl	Pellet	Ge	300	Flow	25	160	28
S	Pellet	Ge	700	Flow	25	160	9

S1.3 ICP-MS – Instrument and analytical details

Samples were analyzed on an Agilent Technologies 8800 Triple Quadrupole inductively-coupled plasma mass spectrometer. The analytical settings were automatically tuned as recommended by Agilent, and operated within normal limits. Masses were analyzed in three replicates, with an integration time per mass of 0.099 seconds. Helium flow was 4.3 mL/min, and the samples were analyzed in high-matrix interference mode to mitigate the deposition of borate in the instrument. Limits of detection and reference materials analyzed alongside samples (AGV-2, BCR-2, and RGM-2) are given in Supp. Table 2.

S1.4 Mineral analyses

All samples received from Egypt were made into thin sections. The shipment of October 2020 was made into 1 inch rounds, however due to a global shortage of round glass slides, the later shipment was made into 27x46 mm rectangular sections by Spectrum Petrographics, Inc. All samples were examined optically and by SEM. 100 of the 129 samples were examined by EPMA.

S1.5 EPMA Methods

F was analyzed for 60 s as the only element on the LDE1 crystal. Standards included a combination of natural and synthetic materials (Supplementary Table 1b). Standards are synthetic unless otherwise noted. Counts were corrected using a mean atomic number background subtraction and the CITZAF matrix algorithm. Spots were analyzed for volatile elements (i.e., F, Na) first, followed by more refractory elements to reduce loss over time.

All elements analyzed with 25 nA beam current, 15 kV accelerating potential, and a ~1 μm focused beam with an on-peak count time as specified in Supplementary Table 1b. Interference corrections were applied to several elements. Detection limits are also provided in this table.

Supplementary Table 4.1b – EPMA Analytical conditions

Spectrometer	SP1	SP2	SP3	SP4	SP5
Diffraction Crystal	LDE1	LiF	PET	TAP	LIF
Element, line Standard	F , $K\alpha$ Fluorophlogopite	Ba , $L\alpha$ BaSiO ₃ glass	K , $K\alpha$ Asbestos Microcline*	Na , $K\alpha$ Amelia Albite*	Mn , $K\alpha$ Mn-olivine
Count time.	60 s	20 s	18 s	20 s	20 s
Corrections	Fe	Sc	U	Zn	none
Det. Lim $\mu\text{g/g}$	272	1280	96	267	281
Element, line Standard		Ti , $K\alpha$ TiO ₂	P , $K\alpha$ ScPO ₄	Mg , $K\alpha$ Forsterite	Fe , $K\alpha$ Fayalite
Count time.		20 s	18 s	20 s	20 s
Corrections		La, Ba	none	Nd	none
Det. Lim $\mu\text{g/g}$		562	266	185	346
Element, line Standard		La , $L\alpha$ LaPO ₄	Zr , $L\alpha$ Pacoima Zircon*	Al , $K\alpha$ Anorthite	Er , $L\alpha$ ErPO ₄
Count time.		20 s	18 s	20 s	20 s
Corrections		Ti	none	Yb	Hf
Det. Lim $\mu\text{g/g}$		1328	516	190	3454
Element, line Standard		Ce , $L\alpha$ CePO ₄	Nb , $L\alpha$ NbO	Yb , $M\alpha$ YbPO ₄	Hf , $L\alpha$ Hf metal
Count time.		20 s	18 s	20 s	20 s
Corrections		Ti, Ba	none	Al	Cu, Er
Det. Lim $\mu\text{g/g}$		1126	486	994	1325

Element, line Standard Count time. Corrections Det. Lim $\mu\text{g/g}$		Pr , $L\alpha$ PrPO4 20 s La 1029	S , $K\alpha$ PbS 18 s Nb 213	Si , $K\alpha$ Amelia Albite* 20 s Hf, Ta 252	Cu , $K\alpha$ Cu metal 20 s Ta 528
Element, line Standard Count time. Corrections Det. Lim $\mu\text{g/g}$		Nd , $L\alpha$ NdPO4 20 s Ba, Ce, Pr 951	Th , $M\alpha$ ThO2 18 s none 366	Sr , $L\alpha$ Synth SrSiO3 glass 20 s Ta 178	Ta , $L\alpha$ Ta metal 20 s Cu 1492
Element, line Standard Count time. Corrections Det. Lim $\mu\text{g/g}$		Sm $L\alpha$ SmPO4 20 s Ce, Pr, Nd, Mn 870	U $M\alpha$ UO2 18 s none 627	Y $L\alpha$ YPO4 20 s Zr, Hf 766	Zn $K\alpha$ ZnO 20 s none 712
Element, line Standard Count time. Corrections Det. Lim $\mu\text{g/g}$		Gd , $L\alpha$ GdPO4 20 s Nd, Ce, Mn 1089	Sn , $L\alpha$ Sn metal 18 s none 260		Pb , $L\alpha$ PbS 20 s Ta, Hf 5519
Element, line Standard Count time. Corrections Det. Lim $\mu\text{g/g}$		Dy , $L\alpha$ DyPO4 20 s Sm, Mn, Fe 12,849	Ca , $K\alpha$ Anorthite 18 s Sn 108		
Element, line Standard Count time. Corrections Det. Lim $\mu\text{g/g}$			Sc , $K\alpha$ ScPO4 18 s Sn 131		

* signifies standard is a natural sample.

S1.6 Raman spectroscopy

Raman analyses of select thin sections were conducted using a Renishaw inVia Raman Spectrometer. The system was calibrated on Si plates and operated using an 1800 mm^{-1} grating, 514 nm laser, and 65 μm slit. Analyses ranged from 1 to 5 passes at 0.1 to 5 % laser power, depending on the target (i.e., less stable samples were analyzed at lower laser power, with more replicates collected to compensate for lower signal resolution). Data was analyzed using WiRE (ver. 5.6) and compared with the RRUFF database and in-house libraries.

S1.7 LA-ICP-MS Methods

One sample (1014D) was analyzed for Li content in the micas using a New Wave Research UP-193 (c. 2007) laser ablation system connected to the same Agilent 8800 ICP-MS used in trace element analysis. The laser was operated at 90% power, 10 Hz frequency, with a spot diameter of 50 μm . The ICP-MS was operated in no-gas mode for these analyses.

There were two sessions. In the first, the thin section was loaded with a brass-mounted chip of NIST SRM 610. ^{58}Fe was used as the internal standard. In this session, a total of 16 spots were analyzed, but due to complications with the laser camera, only 8 of the spots were placed correctly on the mica. In the second, NIST SRM 612 was the calibration standard and ^{28}Si was the internal standard. 9 points were placed, all of which were on mica. The sessions resulted in an average Li_2O wt. % of 4.38 ± 0.12 and 4.49 ± 0.46 , respectively. Error is one standard deviation of the mean.

Appendix IV.2: Results

S2.1 Samples excluded from main text discussion

Whole-rock geochemistry plots are shown in Supp. Figs. 5-8. Mineral data is provided in Supp. Table 4.

Veins and Aplites

The following samples were identified as aplite veins from Abu Rusheid: Skt 14, Skt 18, Skt 19, Skt 20, Skt 23, and NgR51. The majority of these samples were albite and K-feldspar, though they also contain limited amounts of the phases present in the main body. These include quartz, mica, zircon, columbite-(Fe), fluorapatite, and rare-metal phases (monazite-(Ce), xenotime-(Y), rutile, aeschynite-(Y), fergusonite-(Y), fluocerite-(Ce), and pyrochlore). Five of the samples have a very narrow range of chemistry that is very close to pure feldspar: SiO₂ 66.67-68.55 wt.%; Al₂O₃ 18.33-19.31 wt.%, Na₂O 5.77-7.87 wt.%, K₂O 4.82-6.50 wt.%, and all other major elements are <0.5%. One sample has the same range of SiO₂ and Al₂O₃, but has 0.93 wt.% MgO, 0.84 wt.% CaO, and outlier concentrations of Na₂O (10.02 wt.%) and K₂O (0.42 wt.%).

From Abu Dabbab, ADb 19, ADb 20, and ADb 22 are all quartz veins. These are almost entirely quartz, with minor K-feldspar and mica. Accessory phases include cassiterite (with crystals up to 2 cm), monazite-(Ce), and fluorite. The chemistry ranges from 89.01-100.00 wt.% SiO₂, with the remaining percentage primarily Al₂O₃ (0-6.49 wt.%), K₂O (0-3.01 wt.%), and Fe₂O₃ (0-0.70 wt.%).

ADb 21 is a mica cluster. The majority of the mica is F-rich zinnwaldite, coexisting with albite and K-feldspar. It contains topaz, cassiterite, zircon, fluorite, rutile, columbite-(Fe), and pyrochlore as accessory phases. It has a micaceous bulk chemistry, with 39.47 wt.% SiO₂, 42.60 wt.% Al₂O₃, 5.70 wt.% K₂O, and a high LOI of 3.13 wt.%.

Country Rocks at Abu Rusheid

Skt 27: A meta-sedimentary country rock. The mineralogy of this rock includes magnesite-calcite, actinolite-tremolite, and talc, with accessory pyrite. This sample is rich in MgO (31.63 wt.%) and Fe₂O₃ (7.89 wt.%), and is poor in SiO₂ (33.52 wt.%) and Al₂O₃ (3.00 wt.%). Its carbonate-bearing nature is reflected in a high LOI (18.88 wt.%). It shows a low enrichment across all its trace elements. Due to the low CaO content (3.31 wt.%), an appropriate name for this rock would be a magnesian skarn.

Skt 28: A meta-volcanic country rock. The mineralogy includes feldspars, actinolite, micas, chlorite, and fluorapatite. Accessory phases include ilmenite, baryte, goethite, and almandine. It is high in Al₂O₃ (24.50 wt.%), Fe₂O₃ (18.59 wt.%), CaO (7.23 wt.%), and TiO₂ (1.55 wt.%). It also has the highest P₂O₅ observed at Abu Rusheid (0.42 wt.%). It is low in SiO₂ (30.35 wt.%). It is best described as a garnet-bearing chlorite-actinolite metabasalt.

NgR 27: A meta-volcanic country rock containing actinolite, titanite, iron oxide, and quartz. It has a SiO₂ content of 48.91 wt.% and Al₂O₃, Fe₂O₃, MgO, and CaO contents of around 10%, and a high TiO₂ (1.34 wt.%). It also shows a general

low enrichment in its trace element patterns. It is also likely a metabasalt, though a higher grade than Skt28.

Ard 8: A metamorphic country rock made up primarily of phlogopite, with fluorapatite, actinolite, feldspar, and zircon. Its micaceous nature is reflected in its geochemistry, which is primarily SiO₂ (44.58 wt.%), MgO (17.88 wt.%), Al₂O₃ (10.51 wt.%), and Fe₂O₃ (9.91 wt.%), with some CaO (6.53 wt.%) and K₂O (4.23 wt.%). This sample also shows a general low enrichment across most of its trace elements. It appears in hand sample to be a biotite schist.

Ard 22: A metamorphic country rock consisting of actinolite and talc with accessory bastnasite-(Y), minor carbonates, and an undescribed fluorinated yttrium arsenate. This rock is high in SiO₂ (54.46 wt.%), MgO (20.02 wt.%), and CaO (11.15 wt.%), and low in Al₂O₃ (3.49 wt.%). This sample is one of the only ones from this study to not be enriched in most trace elements, with a strong depletion in Hf and Ta not seen in any other samples. It has a very flat lanthanide pattern just above primitive mantle concentrations. This rock could be named an actinolite-talc schist. This sample contains a novel fluorinated yttrium arsenate, Y₂As₂O₇F, likely a new mineral species (to be described elsewhere).

Other Rocks at Abu Rusheid

Skt 29: A highly silicified granite, with evidence of igneous textures in hand sample, but a whole-rock geochemistry of 90% SiO₂, and lesser amounts of Al₂O₃,

Na₂O, and K₂O. In addition to quartz and silicified feldspars, the mineralogy ensemble includes many of the phases seen in the main body of the pluton, including cassiterite, zircon, columbite-(Fe), pyrochlore, and altered Nb-Ti oxides.

Skt 30, Ard33: These rocks are igneous in appearance, but much more mafic than the main body of the granite. Skt 30 is intermediate in appearance with large crystals of quartz, albite feldspar, and dark mica (2-8mm), while Ard 33 is very melanocratic, with the substitution of actinolite amphibole for biotite in the above assemblage. Compared to the main pluton, both show higher MgO (Skt30 0.70 wt.%; Ard33 2.70 wt.%), CaO (Skt30 2.38 wt.%; Ard33 6.60 wt.%), and Fe₂O₃ (Skt30 3.08 wt.%; Ard33 6.59 wt.%). Skt30 is slightly more silicic (SiO₂ of 65.80 wt.%) and sodic (Na₂O of 6.68 wt.%) than Ard33, with respective concentrations of 60.87 wt.% and 3.94 wt.%. From their trace element patterns (Supp. Fig 7c), there are similarities: their enrichment in U, relative depletion in Nb and P, and overall enriched character. However, there are notable differences in their lanthanide behavior. Neither sample displays a Eu anomaly ($Eu/Eu^* = 0.84-1.01$), but Ard33 is flat $[(La/Yb)_n = 2]$ and Skt30 is enriched in LREE $[(La/Yb)_n = 27]$. The accessory phases of Skt 30 include ilmenite, monazite-(Ce), zircon, fluorapatite, and almandine garnet; the mica present here is annite in composition. Ard 33 contains titanite, ilmenite, iron oxides, zircon, and fluorapatite. The feldspars in both of these samples are notably more calcic than the main body feldspars, with average

compositions of $\text{Na}_{0.84}\text{Ca}_{0.15}\text{Al}_{1.14}\text{Si}_{2.87}\text{O}_8$ in Skt 30 and $\text{Na}_{0.68}\text{Ca}_{0.33}\text{Al}_{1.32}\text{Si}_{2.67}\text{O}_8$ in Ard 33. From the variations in major and trace element geochemistry, as well as major and accessory mineralogy, it does not appear these two samples are derived from the same intermediate intrusion (See Discussion below).

Country Rocks at Abu Dabbab

ADb 23: A contact between the granite and another lithology. Unfortunately, the whole-rock chemistry appears to be an average across the boundary, sampling both rocks, and will be disregarded. From the thin section mineralogy, the mafic phase lithology contains amphibole, phlogopite, and plagioclase, with accessory rutile. The felsic lithology contains feldspars, including K-feldspar and plagioclase, and mica, with abundant fluorite. Accessory phases are fluocerite-(Ce), monazite-(Ce), thorite, and thorianite.

ADb 26: A meta-volcanic country rock. The phases present in this sample include augite-diopside and plagioclase, with accessory apatite, ilmenite, and rutile, with secondary iron oxides. The rock is fine-grained with a SiO_2 content of 42.87%, and it is recognizable in hand sample as an altered basalt. Notably, it shows the same relative depletion in Y as adjacent granites.

Appendix IV.3: Discussion

S3.1 Phase Identification: Micas

There are multiple species of mica present at Abu Rusheid and Abu Dabbab, but due to some analytical challenges (i.e., no Li from EPMA data, low totals from OH groups), additional steps were necessary to identify specific phases. Several micas within 1014D were analyzed for Li by LA-ICP-MS, yielding contents of 3.8-5.3 wt. % Li₂O in the ferroan micas. Some authors (i.e., Tindle and Webb, 1990; Tischendorf et al., 1997) demonstrate that Li content of micas correlates strongly with F, SiO₂, MgO, and/or Rb contents, in both di- and trioctohedral micas. Li concentrations calculated according to Tischendorf et al. (1997) do not overlap our measured concentrations within measurement error for 1014D, except using the prediction based F. Estimates of Li are provided in (Supp. Table 5) and a mica discrimination diagram is shown in Supp. Fig. 4.

Whole-rock fluorine and mica F and Fe contents are shown in Supp. Fig 7.

S3.2 Phase Identification: Nb-Ta-Ti Oxides

Many of the rare-metal-bearing minerals present in this pluton proved challenging to identify from their chemistry. To aid in the discrimination of different Nb-Ta-Ti oxide groups (samarskite, aeschynite-euxenite, pyrochlore-microlite, fergusonite), we used the three-group discrimination diagram of Ercit (2005). In this scheme, two variables are calculated from the mineral chemistry:

$$\begin{aligned} \text{CV1} = & 0.245 \text{ Na} + 0.106 \text{ Ca} - 0.077 \text{ Fe}^* + 0.425 \text{ Pb} + 0.220 \text{ Y} + 0.280 \text{ LREE} \\ & + 0.137 \text{ HREE} + 0.100 \text{ U}^* + 0.304 \text{ Ti} + 0.097 \text{ Nb} + 0.109 \text{ Ta}^* - 12.81 \end{aligned}$$

$$\begin{aligned} \text{CV2} = & 0.102 \text{ Na} - 0.113 \text{ Ca} - 0.371 \text{ Fe}^* - 0.167 \text{ Pb} - 0.395 \text{ Y} - 0.280 \text{ LREE} \\ & - 0.265 \text{ HREE} - 0.182 \text{ U}^* - 0.085 \text{ Ti} - 0.166 \text{ Nb} - 0.146 \text{ Ta}^* + 17.29 \end{aligned}$$

In both variables, $\text{Fe}^* = \text{Fe} + \text{Mn}$; $\text{U}^* = \text{U} + \text{Th}$; $\text{Ta}^* = \text{Ta} + \text{W}$; and all variables are in oxide weight percent. The results of this are plotted in Supp. Fig. 3. Due to the extensive alteration present at both localities, including recognizable Pb loss and/or redistribution, as well as no measurements of odd-numbered HREEs (Ho, Tm, Lu) and W, several analytical points are challenging to constrain. In some of these cases, unusually high Pb concentrations are disregarded, and in others, textural evidence was used to identify alteration products and/or aggregates. OH contents are calculated from totals.

At Abu Dabbab, all the complex oxides were within the microlite group, between **fluornatromicrolite** ($\text{Na}_{2.6}\text{Ca}_{2.4}\text{Mn}_{0.4}\text{Fe}_{0.2}\text{Ti}_{0.2}\text{Si}_{1.8}\text{Nb}_{2.3}\text{Ta}_{4.5}\text{O}_{23}\text{F}_{3.7}(\text{OH})$) and **fluorcalciomicrolite** ($\text{Na}_{2.2}\text{Ca}_{2.8}\text{Mn}_{0.1}\text{Fe}_{0.3}\text{Ti}_{0.2}\text{Si}_{1.1}\text{Nb}_{0.9}\text{Ta}_{5.7}\text{O}_{20}\text{F}_{2.9}(\text{OH})_4$).

As with other metrics, the samples from Abu Rusheid are much more variable. Many samples contained minerals that chemically belong to either the aeschynite or the euxenite group (Aes-Eux), but it was not possible to determine whether the grains belonged to the *Pmna* (Aes) or *Pbcn* (Eux) space groups. Following the calculations of Ewing (1974) and Ercit (2005), all but one point are euxenite ($\sum \text{LREE} < 0.326 * \text{Ti} - 0.060 * \text{Nb} + 3.1$ oxide wt.%). However, this definition does not account for fersmite, a euxenite group member with low Ti and high Nb, and so all but one

example in this group are defined here simply as “**Aes-Eux**” and have an average chemistry of $\text{Ca}_{0.3}\text{REE}_{0.8}\text{Y}_{2.1}\text{Nb}_{2.9}\text{Ti}_{4.0}\text{Ta}_{0.8}\text{O}_{19}\text{F}_{0.9}(\text{OH})_5$. The other is a sample of **fersmite**, $\text{Ca}_{3.6}\text{Nb}_{7.0}\text{Ti}_{0.3}\text{Ta}_{0.3}\text{Mn}_{0.2}\text{Fe}_{0.4}\text{O}_{21}\text{F}_{1.2}(\text{OH})_3$. Also present are grains of **fergusonite-(Y)**, with a chemistry of $\text{Y}_{3.3}\text{REE}_{1.9}\text{Ca}_{0.3}\text{Nb}_{5.5}\text{Ta}_{0.3}\text{O}_{20}\text{F}_{1.3}(\text{OH})_4$.

Among the pyrochlore-microlite family, many species are present at Abu Rusheid. They include **fluorcalciomicrolite** ($\text{Na}_{2.4}\text{Ca}_{3.4}\text{U}_{0.5}\text{Nb}_{2.7}\text{Ti}_{1.0}\text{Ta}_{3.9}\text{O}_{21}\text{F}_{3.3}(\text{OH})_3$); **fluornatromicrolite** ($\text{Na}_{3.5}\text{Ca}_{2.7}\text{U}_{0.8}\text{Nb}_{2.8}\text{Ti}_{0.7}\text{Ta}_{3.6}\text{O}_{20}\text{F}_{2.8}(\text{OH})_4$); **fluorcalciopyrochlore** ($\text{Na}_{0.6}\text{Ca}_{2.0}\text{U}_{0.7}\text{Y}_{0.5}\text{REE}_{0.4}\text{Pb}_{0.5}\text{Nb}_{5.1}\text{Ti}_{0.3}\text{Ta}_{1.1}\text{O}_{18}\text{F}_{1.4}(\text{OH})_6$); and **fluornatropyrochlore** ($\text{Na}_{2.6}\text{Ca}_{1.7}\text{U}_{0.8}\text{REE}_{0.3}\text{Pb}_{0.5}\text{Nb}_{6.0}\text{Ti}_{0.4}\text{Ta}_{0.7}\text{O}_{19}\text{F}_{3.1}(\text{OH})_5$). There were also two phases in this group, **fluorytterbianpyrochlore** ($\text{Y}_{1.1}\text{Yb}_{1.3}\text{REE}_{1.0}\text{Pb}_{1.2}\text{Th}_{0.1}\text{U}_{0.2}\text{Nb}_{5.9}\text{Ta}_{0.2}\text{O}_{19}\text{F}_{1.5}(\text{OH})_5$) and **fluoryttropyrochlore** ($\text{Y}_{1.6}\text{REE}_{1.6}\text{Ca}_{0.6}\text{Pb}_{0.6}\text{Th}_{0.2}\text{U}_{0.3}\text{Nb}_{5.1}\text{Ta}_{0.7}\text{O}_{18}\text{F}_{1.1}(\text{OH})_6$), previously undescribed and unconfirmed, respectively.

Several samarskite group minerals are also found here, including **ishikawaite** ($\text{Ca}_{0.4}\text{Y}_{0.4}\text{REE}_{0.6}\text{Fe}_{1.9}\text{Th}_{0.2}\text{U}_{1.5}\text{Pb}_{0.3}\text{Nb}_{5.7}\text{Ta}_{0.5}\text{O}_{24}\text{F}_{1.4}$), which is interpreted to be W-bearing due to a low cation total, **calciosamarskite** ($\text{Ca}_{1.7}\text{Y}_{0.8}\text{REE}_{0.4}\text{Fe}_{1.32}\text{Th}_{0.2}\text{U}_{1.3}\text{Nb}_{5.4}\text{Ta}_{0.5}\text{O}_{24}\text{F}_1$), and **samarskite-(Y)** ($\text{Y}_{1.8}\text{REE}_{1.4}\text{Fe}_{1.2}\text{Mn}_{0.5}\text{Nb}_{6.3}\text{Ta}_{0.5}$). Additionally, a Ti-Fe niobate ($\text{Fe}_{3.6}\text{Mn}_{0.2}\text{Ti}_{3.73}\text{Nb}_{4.5}\text{Ta}_{0.3}\text{O}_{24}$) that plots within the ‘samarskite’ field of Ercit (2005) was identified in a sample, but could not be named.

One sample contained a lead-rich **carlosbarbosaite**, $\text{Ca}_{0.6}\text{U}_{4.7}\text{Pb}_{1.5}\text{Nb}_{4.4}\text{Ta}_{0.2}\text{O}_{22}(\text{OH})_2 \cdot \text{H}_2\text{O}$.

Several samples contained alteration products that resemble pyrochlore, with high Pb and Si concentrations and low analytical totals. These were identified through additional textural inspection.

S3.3 Modelling: Magmatic processes

The major element chemical variations observed in these two plutons cannot be adequately reproduced by liquid line-of-descent crystallization models in rhyoliteMELTS (Gualda et al., 2012; Ghiorso and Gualda, 2015; Supp. Figs. 9-11). The rhyoliteMELTS calculations indicate, however, that several samples are consistent with being multiply-saturated hydrous magmatic liquid compositions. Two samples from Abu Dabbab are saturated in this way, one with alkali feldspar + plagioclase and the other with plagioclase + quartz. From the larger dataset of Abu Rusheid samples, we found 25 multiply-saturated compositions, including those with melt simultaneously in equilibrium with quartz + alkali feldspar, quartz + plagioclase, plagioclase + alkali feldspar, and feldspar + magnetite. The multiply-saturated liquidus points calculated do not form a coherent phase diagram as they have variable chemistries. We note that rhyoliteMELTS does not presently consider the influence of magmatic fluorine. These fluorine-rich plutons were investigated as potential targets for testing the development of a more comprehensive thermodynamic model

that does include fluorine; however, the lack of coherent variation among samples means these plutons will be of limited use in the calibration of a fluorine-bearing magmatic model.

Abuamarah et al. (2023) showed that plutons with linear trends in both major and trace element variation diagrams are best modeled not as liquid compositions along a liquid line of descent but rather as mixtures of evolved liquids and their cumulate phases. However, the current data sets are not suitable for this model because the correlations are so poor. Trace element concentrations predicted by combining mineral-melt partition coefficients with the rhyoliteMELTS fractional and equilibrium crystallization models fail to match the data (Supplementary Figs. 12-14). The peak in the middle of several trace element plots (e.g., Fig. 4c) is challenging to explain by a melt interacting with its cumulate pile; for such a trend to form by fractional crystallization requires a major change in partition coefficients at the peak but it is unclear what major or accessory phase might control such behavior in geochemically distinct elements (e.g., Ba, La, Th, and U). The bimodal trace element distribution evident in Abu Rusheid is also inconsistent with any simple magmatic evolution model. The lack of obvious end-members at either locality also precludes treating them with magma mixing or assimilation models.

Given their intermediate nature, samples Skt30 and Ard33 were used in some of the modelling as potential primary magmas of the larger body (ex. Supp. Fig. 9). However, their true relationship with the main pluton is unclear. Neither was

observed *in situ*, so there is no field evidence to support any given hypothesis. These rocks may represent early crystallization of the magmatic evolution of the main body, forming cumulates as the melt evolved to a more silicic chemistry. They may be xenoliths from the country rock, as there have been many episodes of magmatism in the area, or they may have been mafic magmatic enclaves. In both cases, the difference in lithology between the sample and host may have meant they were preferentially weathered out of the pluton. They also may not have been in the pluton at all, and weathered into the *wadi* from country rocks. Another important consideration is that the two samples may also reflect two different histories (i.e., one is a cumulate and the other is a xenolith).

Given the uncertain nature of the samples, additional samples were also used as the starting composition in MELTS models. These included samples that were multiply saturated or granites with the lowest SiO₂ content (Supp. Fig 13). This was also applied to Abu Dabbab, as there were no more primary samples (Supp. Fig. 14).

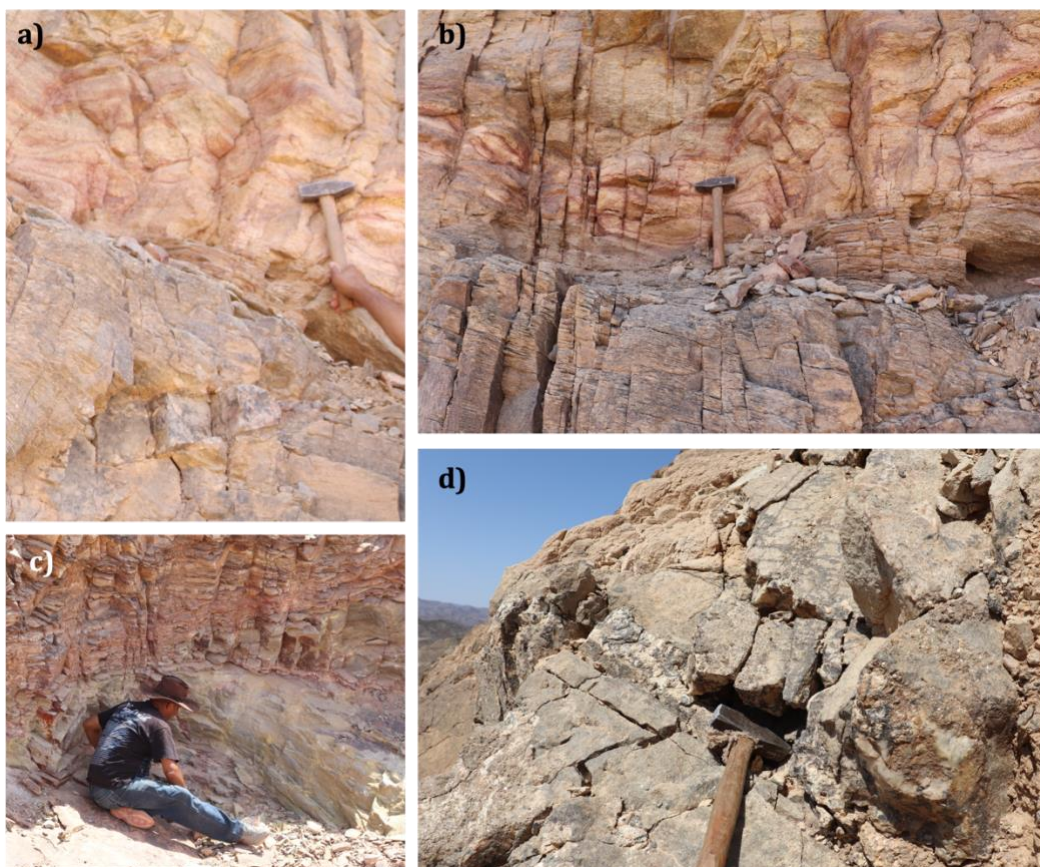
S3.4 Zircon integrity and metamictization (Supp. Fig. 2)

Abu Dabbab: Very few samples contained zircon, which are uniformly euhedral in texture and appearance. AD30 was selected to represent the population. In the Raman spectra collected from this sample, the $\sim 1000\text{ cm}^{-1}$ peak is very broad with a distinct shoulder centered at $\sim 930\text{ cm}^{-1}$, reflecting very strong metamict character. Many of the zircon contained significant U and Th, supporting this interpretation. Most of the

zircons from Abu Dabbab had EPMA totals below 95%, and all contained at least 0.80 wt. % fluorine, which also speak to the non-magmatic character.

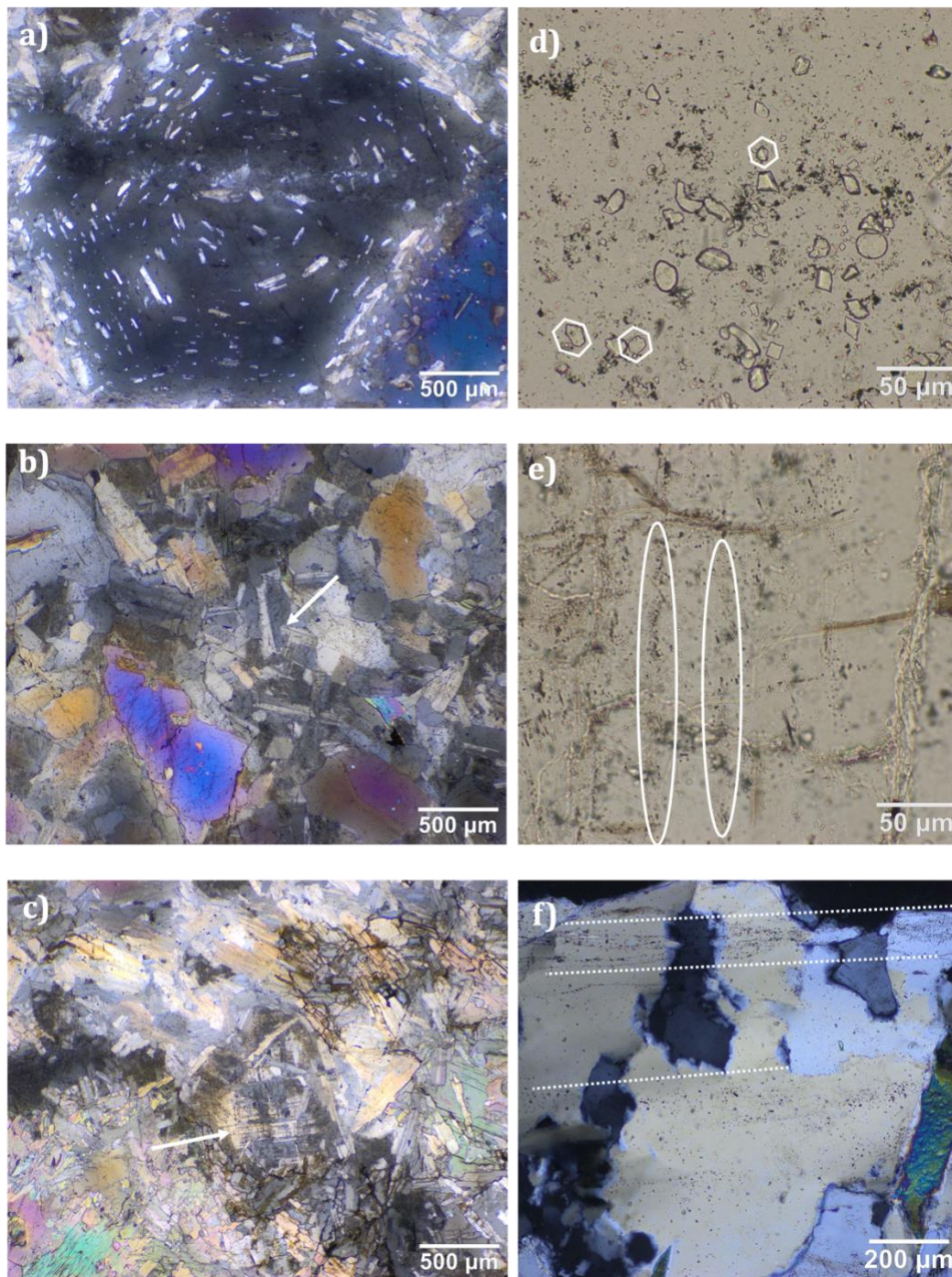
Abu Rusheid: Zircon was present in most of the granitic samples, of several morphologies. NgR37 shows multiple grains with a similar Raman spectrum to the ones collected from AD30, very broad and shouldered. As with Abu Dabbab, the electron probe analyses of the same zircons indicate they are strongly metamict, with low totals, and high U and Th contents. In contrast, the zircons analyzed in Skt31 demonstrated sharp peaks at $\sim 1000\text{ cm}^{-1}$ and $\sim 965\text{ cm}^{-1}$ that are fully mutually resolved from each other. In the thin sections from both NgR37 and Skt31, multiple grains of different orientations were analyzed, as reflected in variation in the lower wavenumber peaks. The character of the $900\text{-}1000\text{ cm}^{-1}$ peaks is consistent across the different orientations.

Supplementary Figures



[Supp. Fig. 4.1](#) – Field photos.

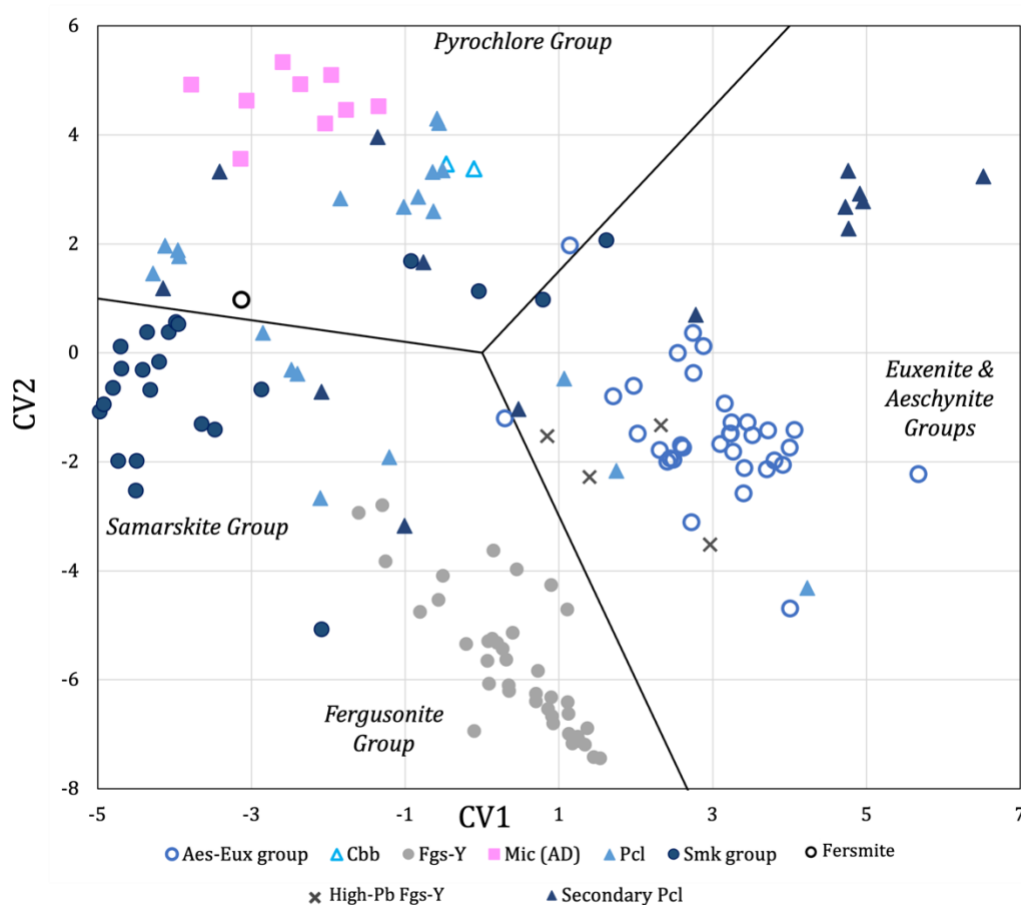
Photographs from Abu Rusheid (a-c) and Abu Dababb (d): a) the contact between the leucogranite (above) and the sheared granite (below); b) the contact between the sheared granite (above) and the country rock (below); c) the site of 3 m deep drill core 1014 in the sheared granite; d) greisen pocket near the top of Abu Dababb.



Supp. Fig. 4.2 – Optical images of thin sections.

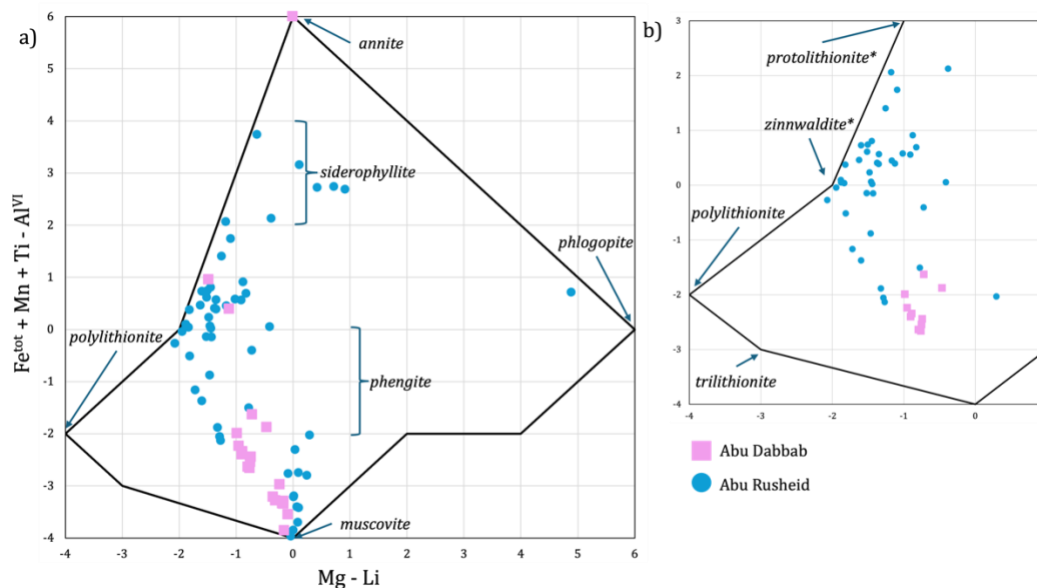
Major petrographic features in major minerals (XPL = cross-polarized transmitted light; PPL = plane-polarized transmitted light): a) snowball quartz in AD30 with

aligned inclusions of plagioclase (XPL); the large grain shows slight undulose extinction; b) albite twins in plagioclase from ADb6 (XPL); the grains here are much more anhedral than the inclusions in a); c) tartan twinning in microcline from AD20 (XPL); d) large primary fluid inclusions in quartz from ADb14 (PPL); the hexagonal outlines emphasize the inverted crystal shapes; e) secondary fluid inclusions in microcline in ADb14 (PPL); the ovals highlight the linear orientation of the inclusions, which run parallel to the twinning observed in XPL; f) trails of secondary fluid inclusions in quartz that traverse multiple grains in Ard27 (PPL).



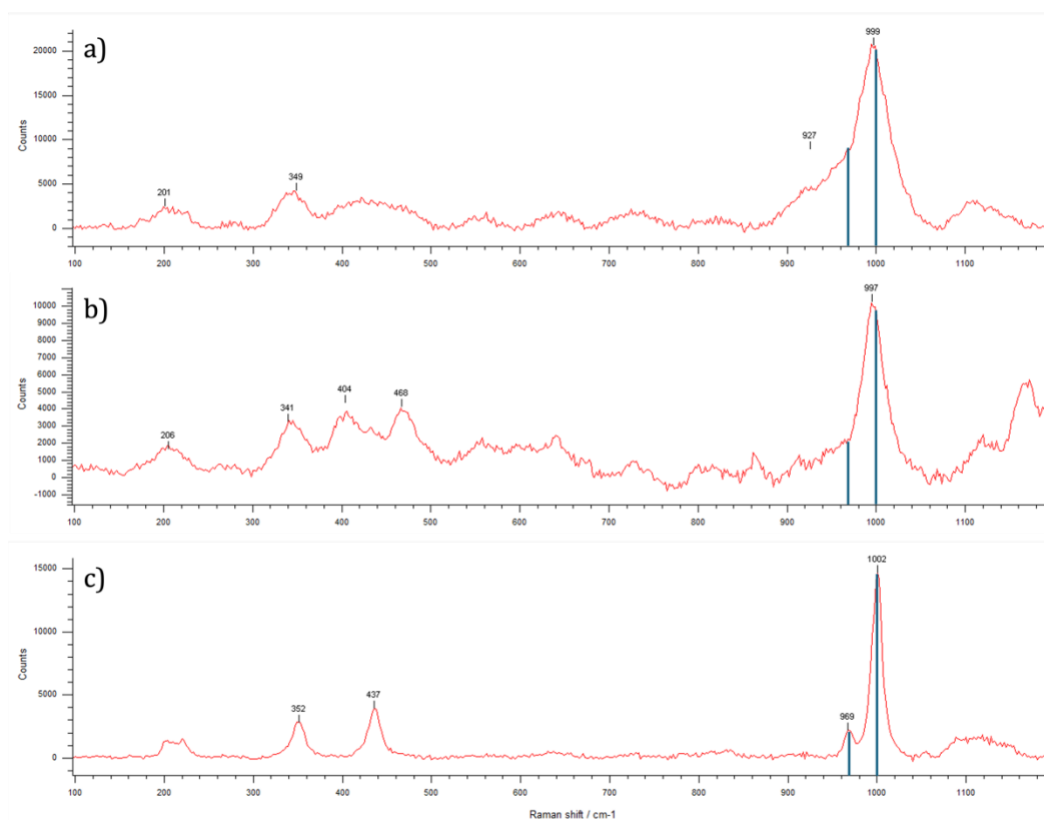
[Supp. Fig. 4.3](#) – Nb-Ta-Ti oxide discrimination diagram of Ercit (2005).

The geochemical parameters “CV1” and “CV2” are calculated as defined in Supp. Text. Most points identified by chemical analysis plot appropriately on this chart, but several may be missing some important components (i.e., W) while others show evidence of alteration (see Supp. Text), resulting in migration away from their primary domain on this chart.



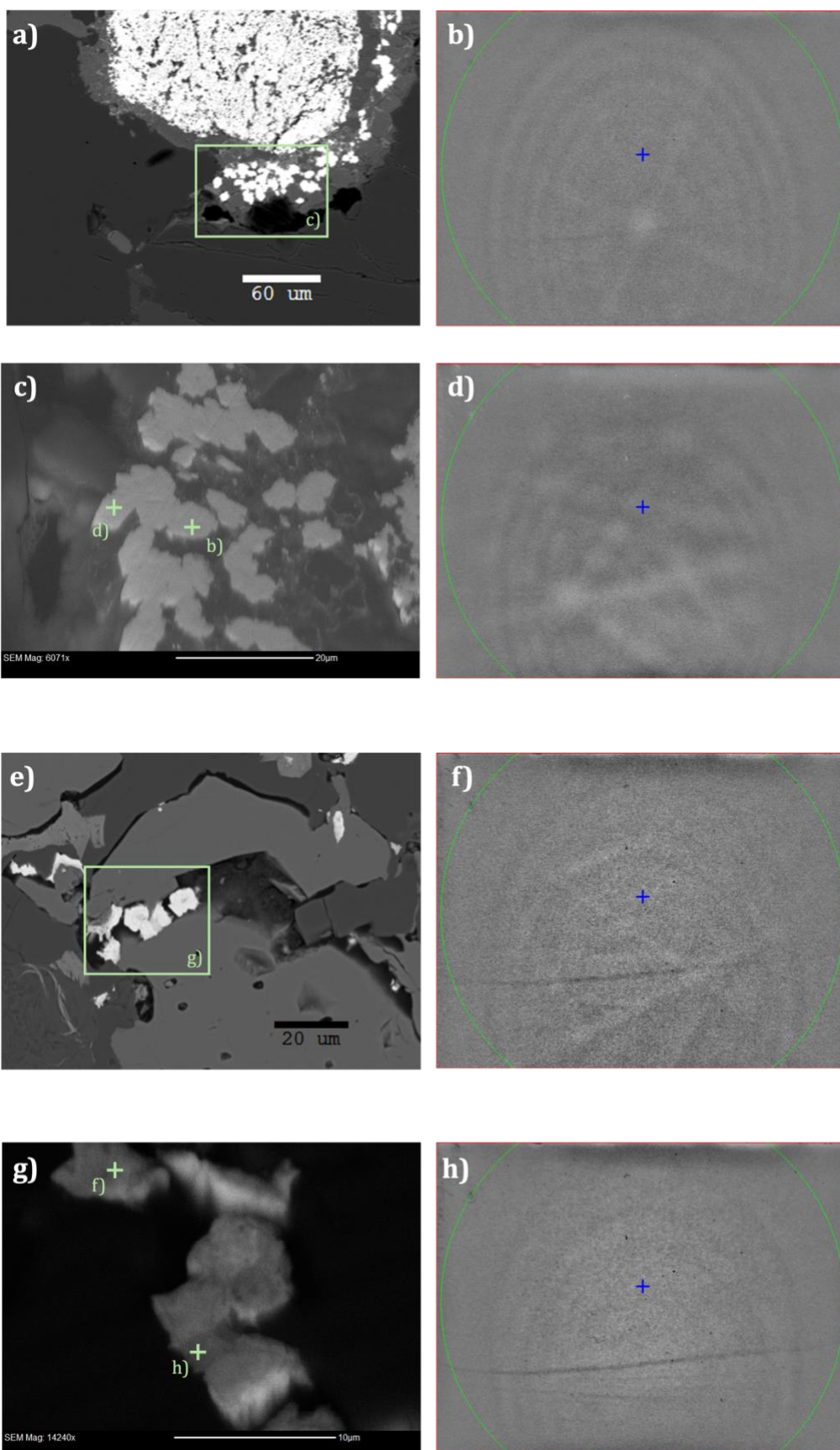
[Supp. Fig. 4.4](#) – Mica classification diagram of Tischendorf et al. (1997)

a) the whole range of mica compositions in Abu Rusheid and Abu Dabbab; b) a narrower focus on zinnwaldite solid solutions. The names are listed according to Tischendorf et al. (1997) for consistency, but note that zinnwaldite and protolithionite are no longer valid mineral species recognized by the IMA. The axes are the same variables in both a) and b).



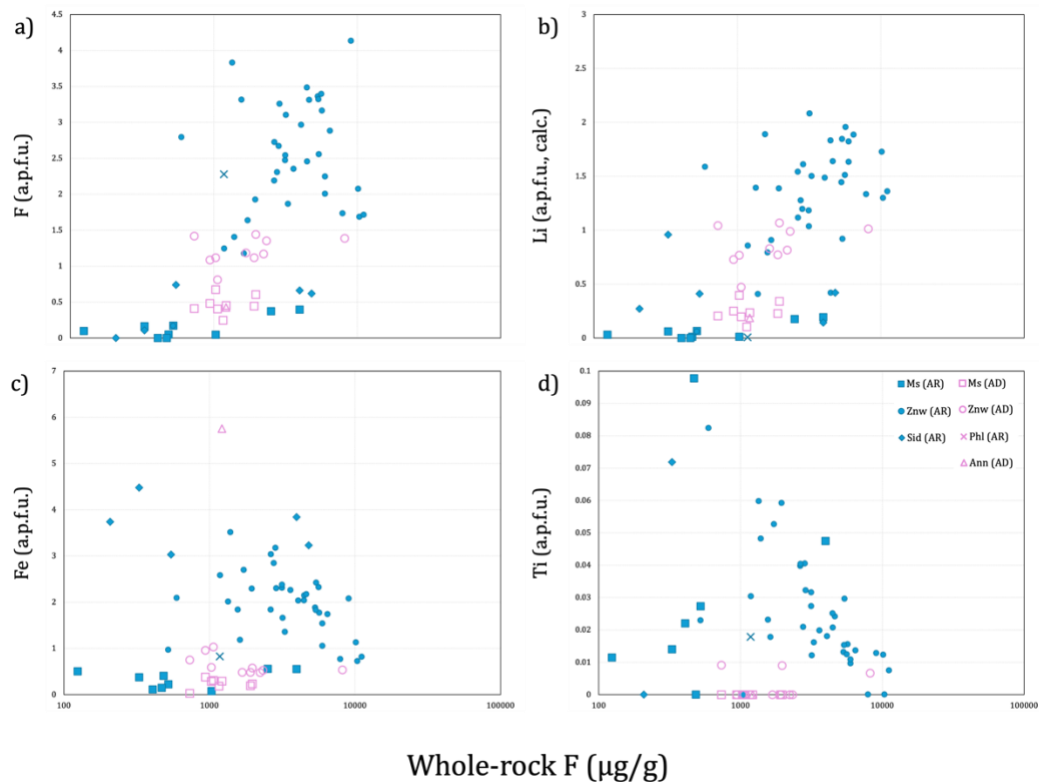
Supp. Fig. 4.5 – Raman shift patterns from zircons in both plutons.

The unresolved shoulder and broad peak at 997 cm^{-1} in small zircons from AD30 (a) resemble those of a similar size from NgR37 (b). However, large zircons from Skt31 (c) have distinct peaks at 967 and 1001 cm^{-1} , indicating a high degree of crystallinity (Geisler et al., 2001). Vertical lines added for clarity.



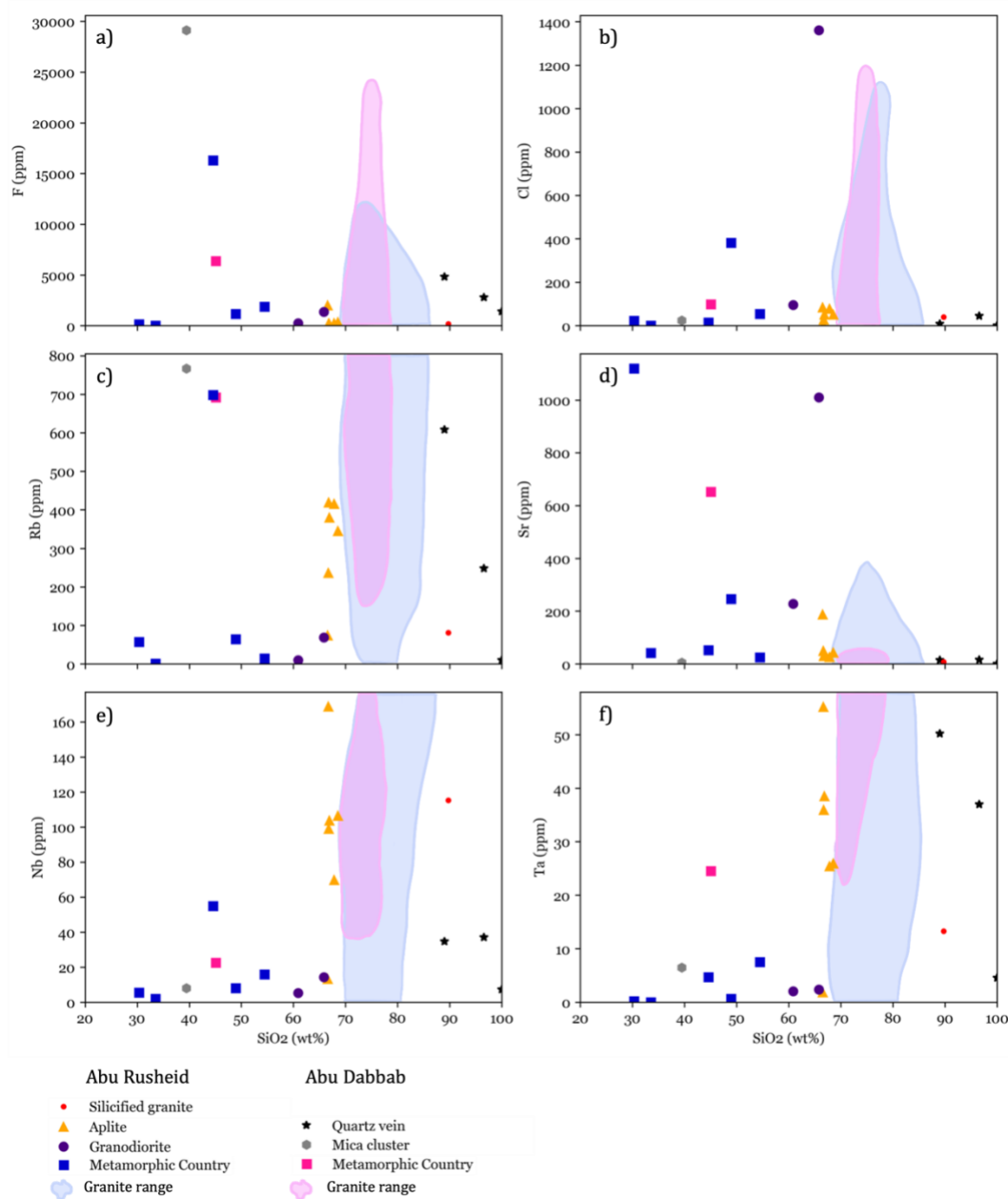
Supp. Fig. 4.6 – Potential new phase morphology and structure.

SEM maps and EBSD analyses of potentially new phases from Abu Rusheid, all of which are beam sensitive. A-d) show an Y-rich thorite from sample 1014A. The high U and Th contents and subsequent radiation damage have rendered the grains poorly crystalline. E-f) show F-rich rhabdophane, a Ca-REE-Th phosphate from Skt22. None of the patterns were resolved enough to index, and the phase identifications specified above are based on EPMA data. a) and e) are BSE images of the areas; c) and g) show the sites of the EBSD analyses; and b), d), f), and h) are the EBSD patterns.



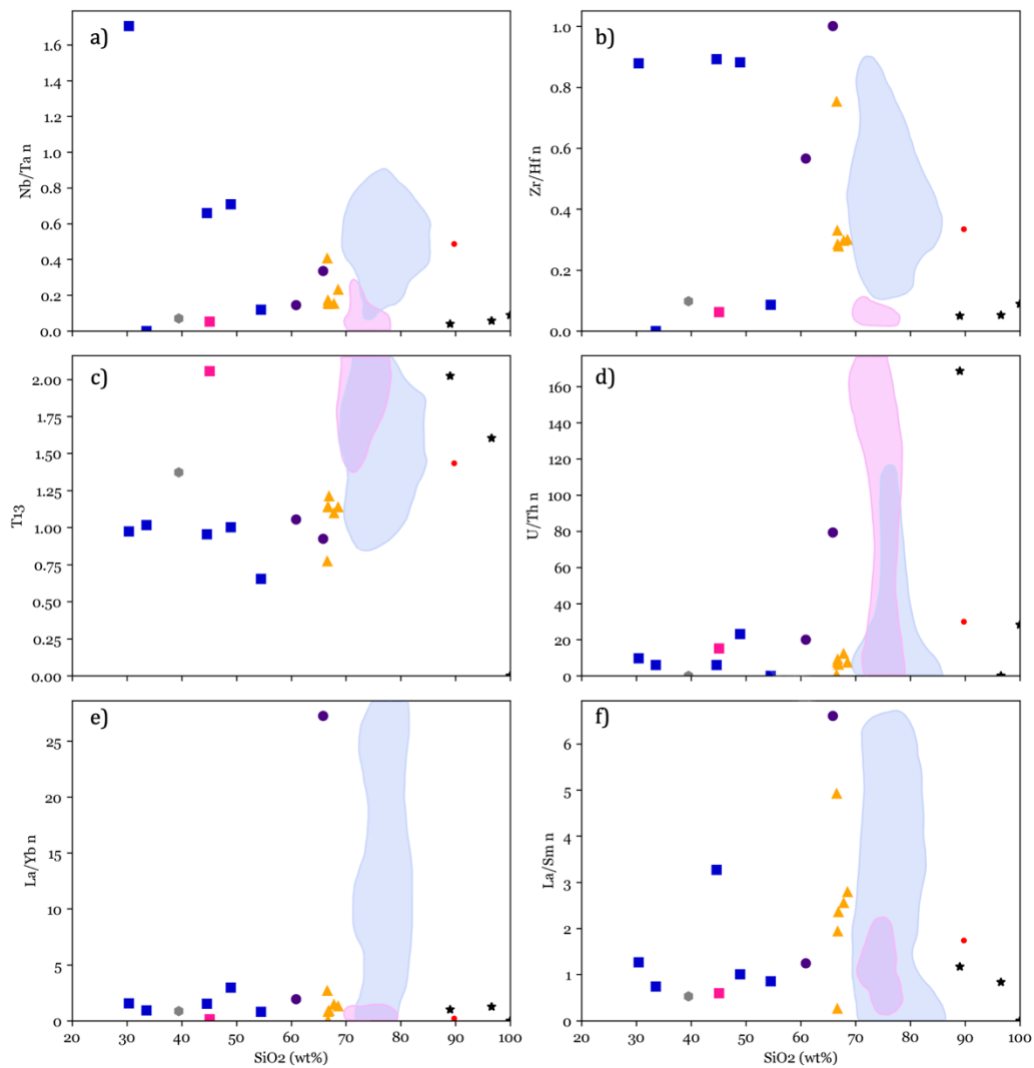
[Supp. Fig. 4.7](#) – Mica composition and whole-rock F.

Whole-rock fluorine concentration versus mica compositional parameters: a) F content, b) calculated Li content, c) Fe content, and d) Ti content (atoms per formula unit, 22 oxygen basis). All species of mica are shown here, with legend given in panel d).



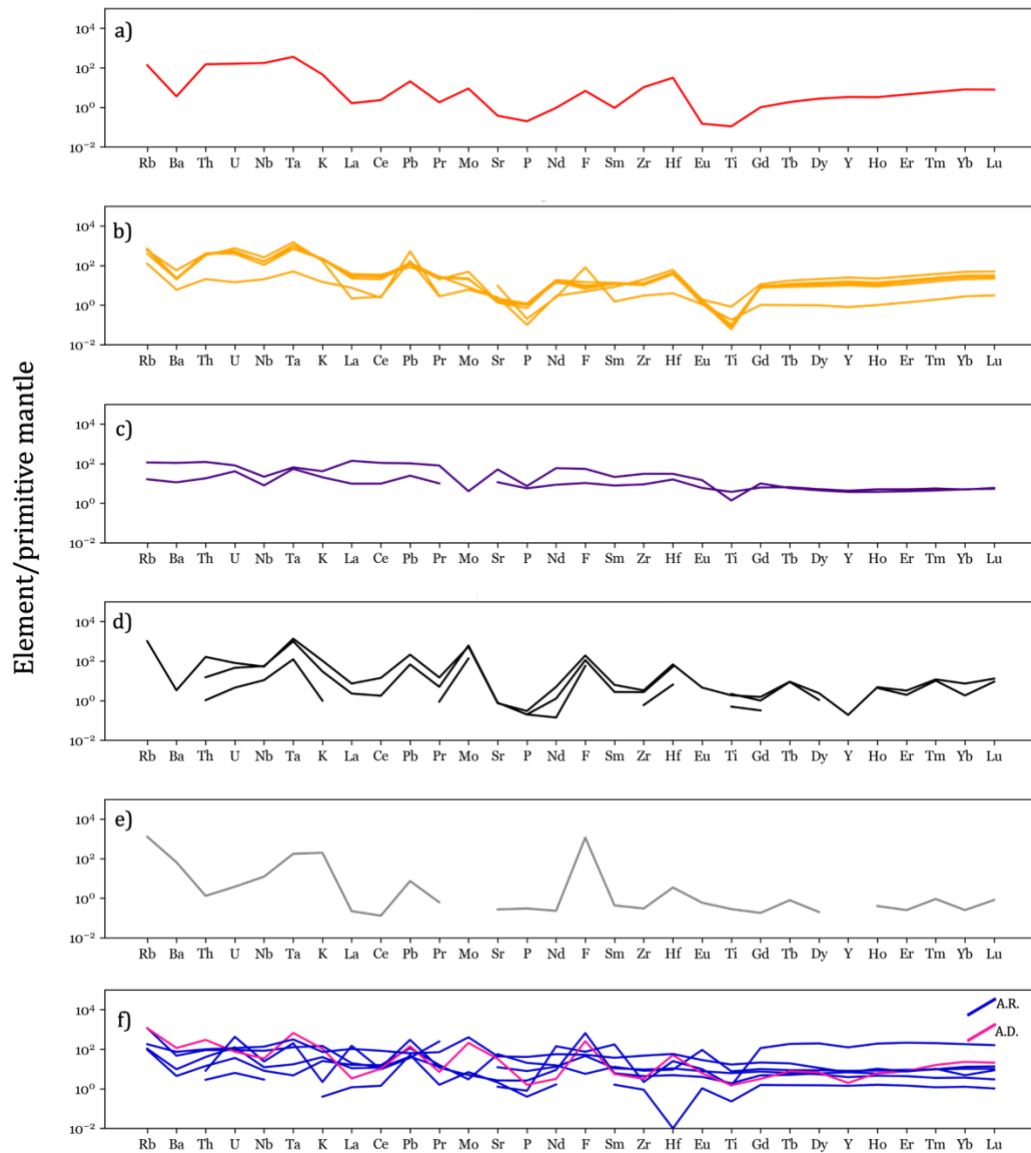
Supp. Fig. 4.8 – Non-granite Harker diagrams.

Select trace element plots of non-granites sampled at both localities: a) F; b) Cl; c) Rb; d) Sr; e) Nb; f) Ta. The range of granite compositions is indicated by the background fields. All non-granites are shown, but some of the granite range is cut-off.



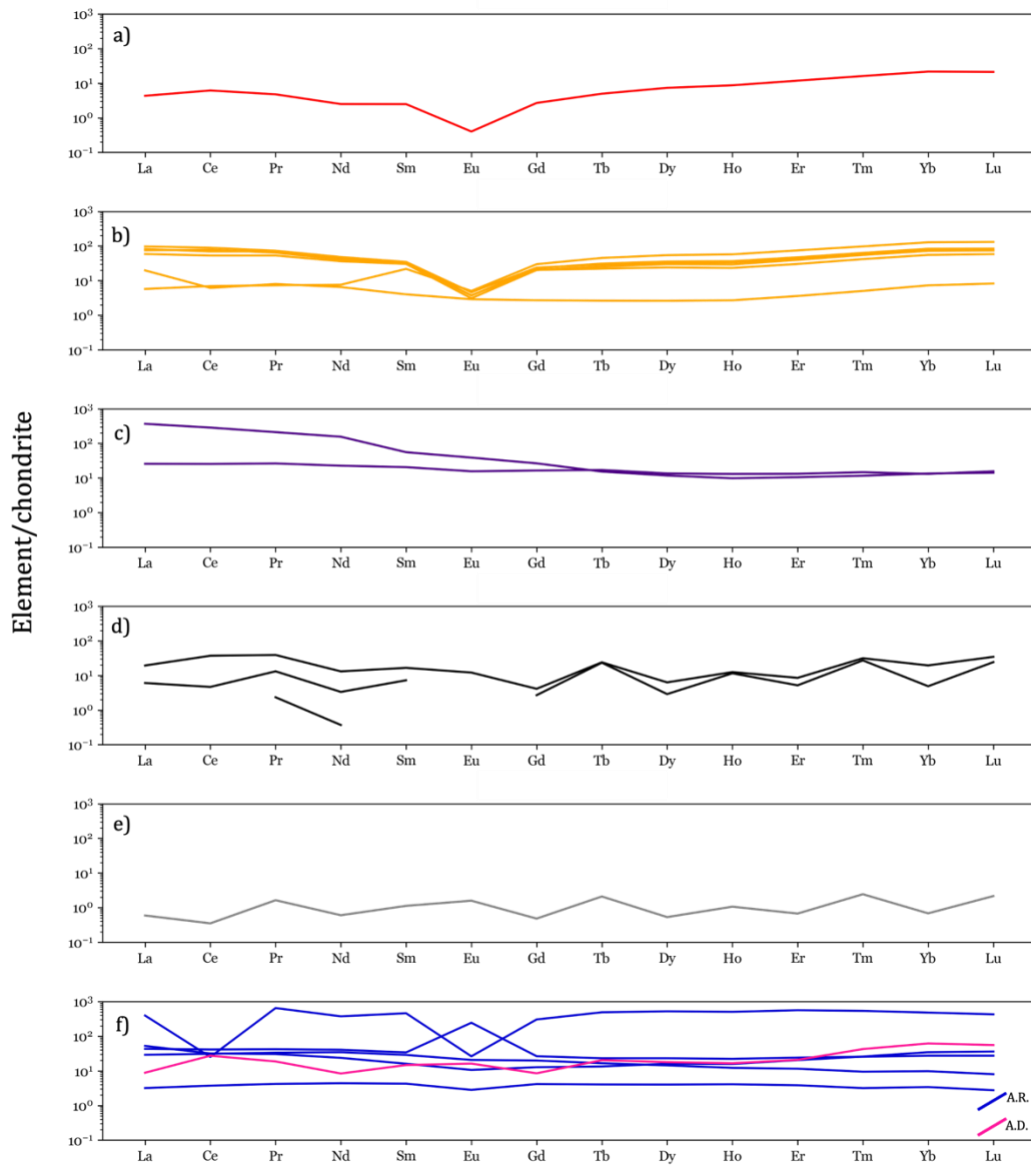
Supp. Fig. 4.9 – Select trace element ratios of non-granites.

a) (Nb/Ta)_n; b) (Zr/Hf)_n; c) $T_{1,3}$; d) (U/Th)_n; e) (La/Yb)_n; f) (La/Sm)_n. All normalization values are from McDonough and Sun (1995). $T_{1,3}$ calculated according to Irber (1999). The range of granite compositions is indicated by the background fields. All non-granites are shown, but some of the granite range is cut-off. Symbols as in Supp. Fig. 4.5.



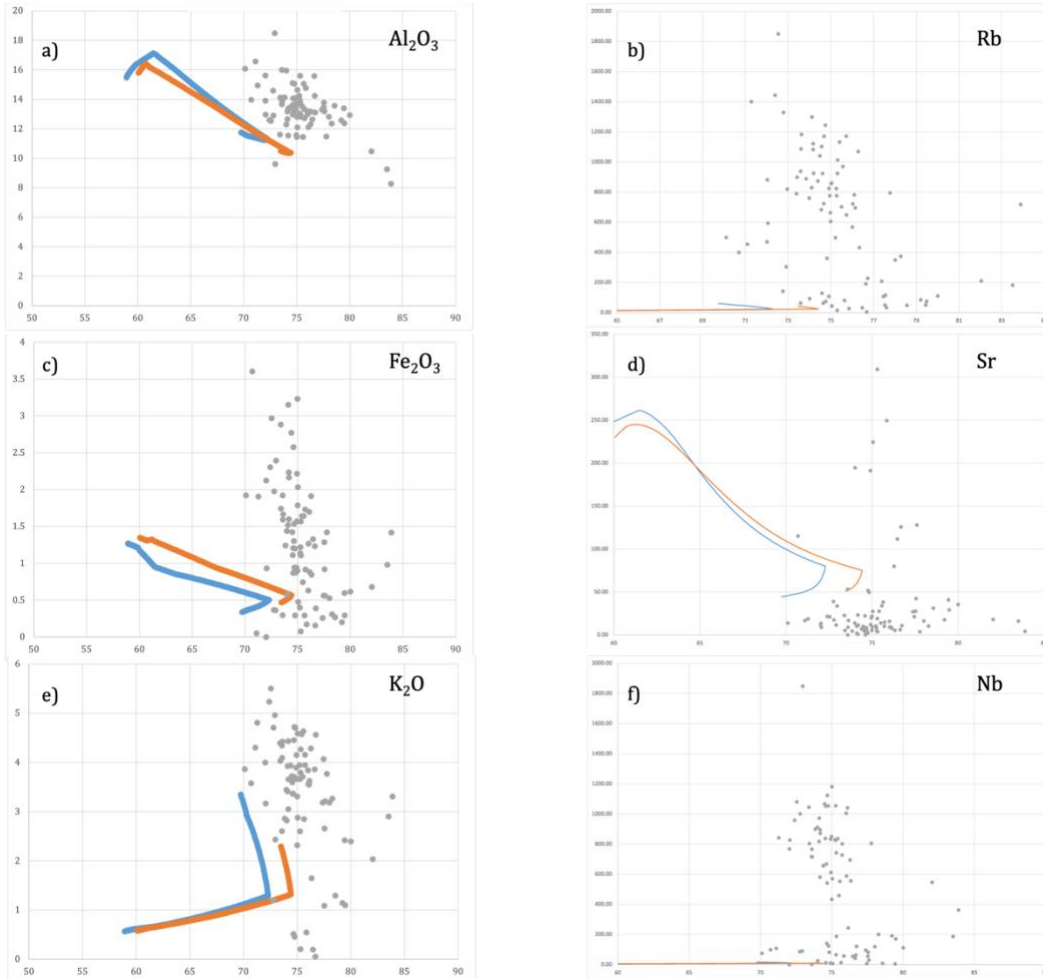
Supp. Fig. 4.10 – Non-granite spider diagrams.

Primitive-mantle normalized multi-element trace element plots for non-granites from both localities: a) the silicified granite from Abu Rusheid (A.R.); b) aplite veins, A.R.; c) granodiorites, A.R.; d) qtz veins, Abu Dabbab (A.D.); e) mica cluster, A.D.; f) metamorphic country rocks from both localities (colors indicated). All vertical axes are the same scale. Normalization values are from McDonough and Sun (1995).



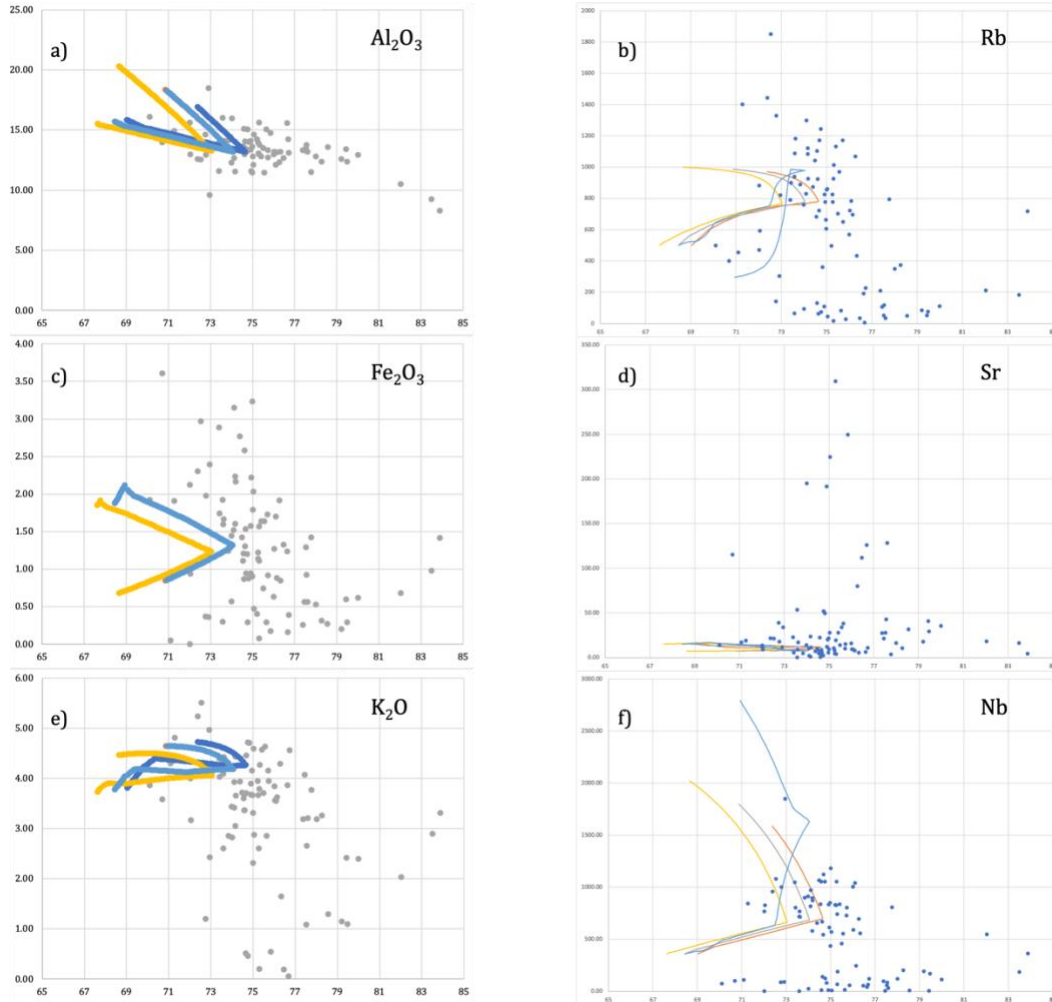
Supp. Fig. 4.11 – Chondrite-normalized lanthanide patterns

Spider plots of of non-granites from both localities: a) the silicified granite from A.R.; b) aplite veins, A.R.; c) granodiorites, A.R.; d) quartz veins, A.D.; e) mica cluster, A.D.; f) metamorphic country rocks from both localities (color indicated). All vertical axes are the same scale. Normalization values are from McDonough and Sun (1995).



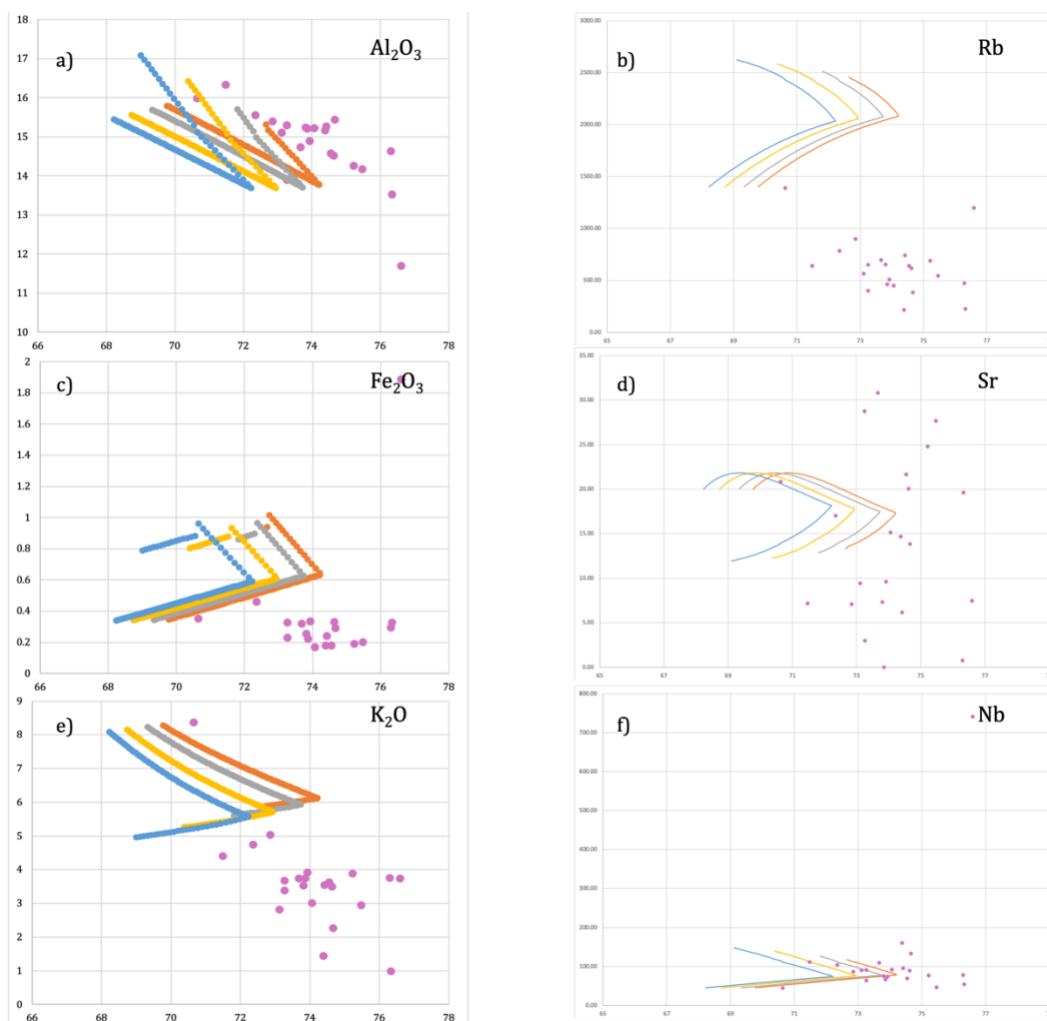
Supp. Fig. 4.12 – Modelling with Ard33.

Examples of attempts to model the fractionation process at Abu Rusheid. This case used primitive granodiorite sample Ard 33 as the starting composition, to test whether other samples could be interpreted as liquids on a liquid line of descent from Ard 33. Trace element concentrations are predicted using mineral/melt partition coefficients and the modal mineral assemblages predicted by rhyoliteMELTS, as in Abuamarah et al. (2023).



Supp. Fig. 4.13 – Modelling with Ard23.

Example of attempts to model the fractionation process at Abu Rusheid. This case used Ard23, the granite with the lowest silica content, as the starting composition, to test whether other samples could be interpreted as liquids on a liquid line of descent from Ard23. Trace element concentrations are predicted using mineral/melt partition coefficients and the modal mineral assemblages predicted by rhyoliteMELTS, as in Abuamarah et al. (2023).



Supp. Fig. 4.14 – Modelling with ADb9.

Example of attempts to model the fractionation process at Abu Dabbab. This case used ADb9, the granite with the lowest silica content, as the starting composition, to test whether other samples could be interpreted as liquids on a liquid line of descent from ADb9. Trace element concentrations are predicted using mineral/melt partition coefficients and the modal mineral assemblages predicted by rhyoliteMELTS, as in Abuamarah et al. (2023).

Appendix IV.4

Supplementary Tables in deposit

Supplementary Table 4.2 – Whole-rock major and trace element data

- 2.1 Major and trace elements for granites
- 2.2 Average for each series and each pluton
- 2.3 Major and trace elements for aplites, veins, country rocks, etc.

Supplementary Table 4.3 – Electron probe data for granites

- 3.1 Summary containing the average mineral composition for each pluton
- 3.2 Quartz
- 3.3 Feldspars
- 3.4 Micas
- 3.5 Garnet
- 3.6 Zircon
- 3.7 F Phases (Fluorite, Topaz, Fluorapatite)
- 3.8 Sulfides (Pyrite, Chalcopyrite, etc.)
- 3.9 Columbite-Tantalite Group
- 3.10 Other Nb-Ta Oxides (Pyrochlore, etc.)
- 3.11 Xenotime-Monazite
- 3.12 Other REE phases (Bastnäsite, Fluocerite, etc.)
- 3.13 Other phases (Cassiterite, Thorite, etc.)
- 3.14 New phase chemistry
- 3.15 Alteration products

Supplementary Table 4.4 – Electron probe data for host rocks

- 4.1 Summary containing the average mineral composition by lithology
- 4.2 Quartz
- 4.3 Feldspars
- 4.4 Sheet silicates
- 4.5 Pyroxene and Amphibole
- 4.6 Other silicates
- 4.7 F Phases (Fluorite, Topaz, Fluorapatite)
- 4.8 Sulfides (Pyrite, Chalcopyrite, etc.)
- 4.9 Columbite-Tantalite Group
- 4.10 REE phases (Xenotime, Bastnäsite, Fluocerite, etc.)
- 4.11 Other phases (Cassiterite, Thorite, etc.)

Supplementary Table 4.5 – EPMA, LA-ICP-MS and calculated Li for micas

Supplementary Figures in deposit

Supplementary Optical and EDS images – labelled figures to show mineralogy and spatial arrangement of all SEM & EPMA regions of interest (ROI) for all thin sections. 129 annotated images.

CHAPTER V

THE BORN-MAYER-HUGGINS REPULSIVE POTENTIAL: A
REVIEW

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Abstract

When running molecular dynamics simulations with force-fields, there are many forms of the interatomic potential. One of the most popular forms of this equation is the Born-Mayer-Huggins equation, which describes the bonding and dynamics of a pair of atoms with a Coulombic term and a repulsive term, which has a large number of free parameters. This includes some variables that are derived from physical quantities, like the characteristic radius of an ion, and purely theoretical terms, like the pre-exponential term. These parameters can be fit to a large number of properties, such as ab initio energy, equilibrium volume, and electric constants. The potentials generated from this form of the equation are not unique, so these other properties are necessary to certify the validity of the parameters used. Once an acceptable description of the potential has been found, there are many properties that can be calculated, including physical descriptions of ion pairs (e.g., bond length), transport quantities of the system (e.g., viscosity), elastic properties (e.g., shear modulus), and more. This review summarizes the forms, values, and analytical assumptions of 50+ publications, including their approaches and the quantities determined with the derived equation.

Introduction

There are many formulations of the atomic interaction potential that may be used in molecular dynamics. The full form of the potential:

$$U_{ij-total} = U_{ij-Coulomb} + U_{ij-Repulsive} + U_{ij-other} \quad (1)$$

generally includes a Coulombic term and a repulsive term, with additional possible terms to represent the van der Waals interactions, the polarizabilities, second-nearest-neighbor interactions, steric effect, and so on. In this formalism, all the possible many-body effects that cannot be reduced to a pair potential are grouped into the “other” term, which implies that the “other” term cannot be represented exactly with any pair-wise calibration.

The repulsive component of the potential describes how overlapping atoms repel each other, preventing the distance between attractive ions from reaching zero. It is commonly represented by an exponential function with several parameters that can be tuned to approximate the ab initio or experimental behavior of atom pairs. This representation is frequently referred to as the Born-Mayer-Huggins or BMH equation. However, there are many names for the BMH equation. Sometimes it is referred to using sub-selections of the three names, including Mayer-Huggins or Born-Mayer, though this has little to do with the individual contributions of the respective scientists. Others refer to this formulation of the interatomic repulsive potential as the Fumi-Tosi (FT) potential due to their work in fitting the Mayer-

Huggins form to the Born model (1964a, b). There are also several later publications (Busing 1972; Ida 1976) that have inspired further names for similar or identical forms of the potential, such as the Gilbert-Ida-Busing (GIB) potential and similar sub-selections of the authors (e.g., Gilbert-Ida). A simplified version of the potential that reduces the parameterization is commonly referred to as the Buckingham or Delaye potential, popularized by van Beest, Kramer, and van Santen (BKS; 1990), although many other authors still refer to this form as the BMH equation.

Of course, there are numerous notation styles for writing the equation. For example, to express the characteristic separation parameter, Ida uses ρ_i (1976), Matsui uses a_i (1982), Fumi & Tosi use r_+ (1964a, b), Gruenhut et al. use σ_i (2005). For ease of comparison, the following notation will be used for the interaction of atom types i and j :

- A_{ij} = pre-exponential term
- $B_{ij} = A_{ij} \exp(\sigma_{ij}/\rho_{ij})$ = Buckingham preexponential term
- ρ_{ij} = hardness (or softness) parameter of the pair
- ρ_i = hardness of atom i in an additive treatment of ρ ($\rho_{ij} = \rho_i + \rho_j$)
- ρ_0 = universal hardness parameter
- σ_i = characteristic ionic radius of atom i

- σ_{ij} = characteristic separation of the pair
- r_{ij} = radial separation of atoms
- q_i = effective charge of atom i

In addition, unless otherwise specified, all energy units will be reported in kcal/mol, all lengths in Å, all times in fs, all temperatures in K, and all masses in grams/mol, per the real units exported by LAMMPS.

Forms of the equation

The range and variation in naming conventions stems, in part, from the differences in approximations and assumptions made when using a particular form of the equation. For example, the BMH form of the repulsive potential usually includes three tunable parameters for the interaction of atoms I and j : A_{ij} , ρ_{ij} , and σ_{ij} . The Buckingham form has two: B_{ij} and ρ_{ij} . The GIB formulation also has two (ρ_{ij} and σ_{ij}) and the pre-exponential is equal to a force constant times ρ_{ij} . As noted above, some authors may use the B_{ij} or $f_0 \times \rho_{ij}$ formulations while still referring to the equation as the BMH equation. Each of these parameters will be discussed in the following section.

The most common forms of the repulsive potential appear in Table 1 below. All of these forms are frequently used.

Table 5.1 – Common forms of repulsive interatomic potential

Name of potential term	Repulsive term: $U_{Repulsive}$
Born-Mayer-Huggins (BMH)	$A_{ij} \exp(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}})$
Buckingham, Delaye, or van Beest-Kramer-van Santen (BKS)	$B_{ij} \exp(\frac{-r_{ij}}{\rho_{ij}})$
Gilbert-Ida-Busing (GIB) or Habasaki	$f_0(\rho_{ij}) \exp(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}})$
Busing or Fumi-Tosi (FT)	$b * \beta_{ij} \exp(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}})$

History of the Potential and Major Publications

There are several groups that have done significant work in select elemental compositional spaces. The initial focus, including the pioneering work by Tomi and Fusi, was on binary alkali halides (Na, K, Rb, Cs and F, Cl, Br, I; 1964a & b). The emphasis on halides was partially due to the abundance of experimental data, including electron distribution maps, compressibility, coefficient of thermal expansion, cohesive energy, etc. The simple structure of NaCl-type halides also facilitated the validation of force-fields. Further work was done to expand to other halide systems, including complex halides (e.g., Li_2BeF_4 by Busing, 1972), or to use the original Fumi-Tosi parameters to evaluate new properties (Ciccotti et al., 1976).

In 1976, there were several foundational publications. These include works by Ida, by Sangster & Dixon, and by Woodcock, Angell, and Cheeseman. Ida (1976) explored the reparameterization of ρ as an additive property and Sangster & Dixon (1976) introduced polarizable ionic potentials, as well as a reevaluation of the Fumi-

Tosi parameters. Woodcock et al. (1976) applied the BMH potential to silica, marking the first use of oxygen as the anion. The Sangster group continued to evaluate the validity of the BMH potential (1978a, b), focusing on the halide system, while Soules (1979) published one of the first complex silicate glass simulations.

The 1980s and 1990s saw a large increase in the number of independent labs publishing data relating to the BMH potential. Of particular note are the works by Matsui (e.g., 1982, 1994) in the silicate space (Na-Ca-Mg-Al-Si-O), Janssen & Tissen (1990) in the carbonate space (K, Na, Li – CO₃), Habasaki & Okada (1992) in the alkali silicates (Li-Na-K-Si-O), Delaye et al (1996) in an oxide space (Na-B-Zr-Al-Si-O), and Belashchenko (e.g., 1992, 1995) in oxides, fluorides, and oxyfluorides (Na-Ca-Al-O-F). In addition, Hirao and Kawamura published the values for many pair interactions in their textbook (1994), which became a reference still in use today.

With the advancement of computational abilities in the 21st century, the field has continued to grow. Many authors now have the inexpensive ability to evaluate new parameters and expand the compositional space further, such as Guillot & Sator (2007; Na-K-Mg-Ca-Ti⁴⁺-Fe²⁺-Fe³⁺-Al-Si-O). More of these simulations can be run for longer periods of time (e.g., LAMMPS, Thompson et al., 2022), allowing for more precise computation of transport or thermal properties. There are several papers that have reviewed differences in potentials between research groups. Parker (1987) focused on the Angell and Hirao groups, in the compositional space of (Li-Na-Al)-

Ba-Zr-F. Bauchy (2014), on the other hand, compared the Matsui, Bouhadja-Jakse, and Delaye groups, which have examined compositions involving Ca-Al-Si-O. A review by Pedone et al. (2022) broadly summarizes some of the above, along with discussions of other possible potentials.

As of the time of writing, there is no single ‘best’ approach when using the BMH potential. However, most authors who do not fit their own parameters use the ones provided by the Hirao & Kawamura group (e.g., Du et al, 2022; Sasaki et al., 2003; Wang et al., 2021) or the Matsui group (e.g., Alderman et al., 2014; Wang et al., 2020). The exact parameter values given in the pioneering work by Fumi & Tosi in 1964 are no longer used by default, as few modern papers study the simple halides. If combining the estimated parameters for a complex simulation, care must be taken to ensure the different cited studies have made comparable assumptions and simplifications.

Parameters

Sigma (σ)

σ is by far the most consistently defined parameter in the potential. It is the characteristic ionic radius of an ion, occasionally referred to as the basic radius (Fumi & Tosi, 1964a). It is similar in value to the crystal or effective ionic radius, as well as the Van der Waals radius for anions. Thanks to these well-known values, the searchable range during fitting for σ is very well constrained. Σ_{ij} is agreed to be an additive property, meaning that for a binary compound, there are Only two σ values

(σ_i and σ_j) which may be combined to yield all three interaction parameters (σ_{ii} , σ_{ij} , σ_{jj}).

For example, σ_{Na} is reported to be between 0.981 and 1.457 Å, although the majority of fitted values are between 1.18 and 1.27 Å, while the known crystal radius of Na is 1.16 Å (Shannon 1976). Similarly, σ_F is generally found to be between 1.21 and 1.57 Å, close to both the crystal radius value of 1.19 Å (Shannon 1976) and the Van der Waals radius of 1.50 Å (Batsanov 2001). A complete list of σ_i and σ_{ij} values used by the references in the compilation is presented in Supplementary Tables 1a and 1b, respectively, and a graphic illustrating the effects of different σ_{ij} values on the ionic potential is shown in [Figure 5.1a](#). As expected, a larger characteristic separation pushes the points at which the potential becomes attractive to larger distances.

Rho (ρ)

ρ is the hardness or softness parameter. Higher values of this variable indicate softer, or more compressible ions, resulting in shallow slopes in the repulsive potential. Conversely, smaller or harder values yield sharper repulsions. The effect of different ρ values on the shape and placement of the total ionic potential can be seen in [Figure 5.1b](#), where it is clear that when all other parameters being held constant, ρ also affects the distance at which the potential switches from repulsive to attractive.

In the original Fumi-Tosi formulation, ρ is a fixed parameter for the family of NaCl-type alkali halides (1964a) or for a given ionic crystal (1964b). While useful in the

binary halides, this makes the potential nonportable (i.e., a ρ_{ij} fit to experimental data for NaCl would not inform the ρ_{ij} used for Na₂O).

Later work by Ida (1976) and Shanker & Agrawal (1980) showed that ρ may be treated as an additive property (i.e., ρ_{Na} from NaCl can be used as ρ_{Na} for Na₂O). This approach arises from the assumption that the cation-cation term and anion-anion term should not be equal, as anions are much more compressible than the cation (Shanker & Agrawal, 1980). For example, they derived a ρ_{Na} of 0.08 Å and a ρ_{Cl} of 0.236 Å, yielding a ρ_{+-} of 0.316 Å, almost identical to the $\rho_{Na-Cl\ xtal}$ used by Fumi & Tosi of 0.317 Å (1964b). However, where Fumi & Tosi would also use 0.317 Å for both ρ_{Na-Na} and ρ_{Cl-Cl} , Shanker & Agrawal argue that the respective values should be 0.159 Å and 0.742 Å. Although this additive treatment of ρ appears to compound the issues of fitting, it reduces the problem in multi-component spaces, as instead of requiring ρ to be dependent on every binary interaction, it establishes that ρ may be established once per atom type, similarly to σ .

Other groups took the simplification further and found that ρ is invariant (or nearly invariant) across all atom pairs, leading to the $\rho_{ij} = \rho_0$ approximation (usually 0.29 Å; Busing, 1972; Woodcock et al., 1976; Soules, 1979). The origin of this assumption follows one of the approaches of Fumi & Tosi (1964a). Some research groups within this camp use a separate parameter for ρ_{O-O} (Delaye & Ghaleb, 1996), or a fixed ρ_i for all cations and a separate value for anions (e.g., Huang et al., 2022), yielding a limited range of ρ_{ij} values across the pairs.

Regardless of the approach or simplifications taken when determining ρ_{ij} , it has a limited range of possible values. It is a positive number less than 0.5 Å, generally between 0.05 and 0.30 Å. Note that some authors (Sangster, 1976; Chen et al., 2021) report the parameter in Å⁻¹ units as $1/\rho_{ij}$, often notated as α_{ij} . For ease of comparison, all values reported have been converted to ρ in Å, as defined in the original papers (Supplementary Table 1; Fumi & Tosi, 1964a).

The pre-exponential

As mentioned above, A_{ij} or, the pre-exponential term more broadly, may be treated with multiple approaches. It is frequently calculated as a function of ρ_{ij} , as a function of σ_{ij} and ρ_{ij} , as a constant times the Pauling factor, as an independent parameter, or as a function of some combination thereof. This coefficient does not necessarily have a physical meaning and instead serves as a tunable coefficient for the whole repulsive term.

The Pauling factor, β_{ij} , is defined as $(1 + z_i/n_i + z_j/n_j)$ where z_i indicates the nominal charge of ion i and n_i is the number of outer-shell electrons (usually 8; Pauling, 1928).

In the original formulation of the potential, the preexponential was denoted as $6 \times \beta_{ij} \times b$, calculated for multiple values of b , an arbitrary constant (Fumi & Tosi, 1964b). This form was simple when applied to alkali halides, as the Pauling factor is 1 for all cation-anion pairs, excepting those involving Li. B was treated as a tunable constant, at the cost of fixing ρ to each crystal. Later authors worked to parameterize

the preexponential in terms of other variables, leading to the $f_0 \times (\rho_i + \rho_j)$ definition (e.g., Habasaki, 1991), where f_0 is unity in force units to convert the distance to energy. In the case of the Buckingham form of the potential, the preexponential B_{ij} is equivalent to $A_{ij} \exp(\sigma_{ij}/\rho_{ij})$. In publications that use this form, take note that A_{ij} cannot be extracted as σ_{ij} is not separately defined. Some authors combine the above methods, leading to more complicated treatment of the preexponential factor, like $A_{ij} = \beta_{ij} \times f_0 \times \rho_{ij}$ (Ida, 1976), $A_{ij} = \beta_{ij} \times b \times \rho_{ij}$ (Shanker & Agrawal, 1980), and $B_{ij} = \beta_{ij} \times \exp(\sigma_{ij}/\rho_{ij})$ (Gruenhut et al., 2005).

A direct result of the different definitions of A_{ij} is that reported values vary up to several orders of magnitude. For example, the A_{Si-Si} determined by Bouhadja & Jakse (2013) is 0.028 kcal/mol, while the same parameter reported by Delaye & Ghaleb (1996) is 10.17 kcal/mol. This, combined with the lack of physical meaning of the parameter, leads to the unfortunate reality that when fitting this coefficient, the search is weakly bounded.

An additional complication is that there are multiple ways to approach the interactions of similarly-charged pairs. A popular approach among authors is to treat A_{ij} as zero for all cation-cation interactions, allowing the ionic potential to be determined solely by electrostatics (e.g., Belashchenko et al., 1998; Guillot & Sator, 2007; Lewis & Catlow, 1985). Some authors evaluate the cross-cation terms by averaging the coefficients (i.e., $A_{ij} = \frac{1}{2} [A_{ii} + A_{jj}]$ when i and j are both cations; e.g., Janssen & Tissen, 1990; Lucas et al., 1984; Jabraoui et al., 2016) or assigning the

same coefficient to all cation-cation pairs (Damodaran et al., 1990). Authors using the GIB or FT formulations are not confronted with this decision.

The effects of different A_{ij} on the shape of the pair potential are shown in [Figure 5.1c](#); the effect of varying this parameter in isolation is seen to be rather similar to the effect of varying r in isolation. Note that the A_{ij} of the middle curve “0.3” has been set to equal to ρ_{ij} (i.e., approximating the GIB formulation). A summary of reported pre-exponential terms is presented in Supplementary Table 1b. The equivalent simplified pre-exponential (B_{ij}) has been calculated for ease of comparison to publications using the Buckingham potential.

To summarize, the pre-exponential approaches include:

- A_{ij} is an independent parameter (tunable), ex. Bouhadja & Jakse (2013)
- A_{ij} is a function of the Pauling factor (fixed) and a constant b (tunable per system), ex. Fumi & Tosi (1964a)
- A_{ij} is a function of ion hardness (tunable per element, not per bond), ex. Matsui (1996)
- A_{ij} is a function of ion hardness (tunable per element, not per bond) and the Pauling factor (fixed), ex. Ida (1976)
- B_{ij} is an exponential function of ion hardness and radius (tunable per element, not per bond) and a constant (tunable), ex. Lewis & Catlow (1985)

- B_{ij} is an exponential function of ion hardness and radius (tunable per element, not per bond) and the Pauling factor (fixed), ex. Gruenhut et al. (2004)

For cation-cation interactions specifically, there are also the options:

- A_{ij} is zero (fixed), ex Guillot & Sator (2007)
- A_{ij} is the average of A_{ii} and A_{jj} (tunable per element, not per bond), ex. Janssen & Tissen (1990)
- A_{ij} is a single parameter (tunable per system), ex. Damodaran et al. (1990)

It should be noted that cation-cation behavior governed by electrostatics only ($A_{ij}=0$) is not satisfactory for elements with low field strength like Na and K, despite widespread usage of this method. The potential is significantly less repulsive when omitting the BMH term ([Figure 5.2](#)), and this results in impractical ion separation lengths. This was not observed to be the case for ions like Si, as the higher charge provides a stronger repulsion in the Coulombic term. Even though the repulsion is not as steep as the BMH potential, it is high enough to reproduce realistic separations.

Additional parameters

Effective charge

It is well established in physical chemistry that the formal charge on an ion in a crystal is not necessarily the best characterization of its electronic behavior (e.g., Matsui, 1994). Although some publications still use the nominal charge (e.g., 4+ for Si; Delaye & Ghaleb, 1996), many authors opt to use effective charges in the Coulombic term of the potential (e.g., 1.890 for Si; Matsui, 1994). In the latter cases, the effective

charge is fit as a free parameter, most often subject to the constraint that the system remain neutral given its stoichiometry. In some cases, the effective charges of all ions in the system are treated with a single scaling factor (e.g., $q_{Ca} = -q_O = 0.5q_{Si}$; Matsui 1994), but other authors accommodate variable effective charges (e.g., $q_{Ca} = 2$, $q_O = -1.4$, $q_H = 0.6$; Hauptmann et al., 2003). It is possible to transfer the effective charges evaluated in other programs for use in the BMH equation (e.g., Hauptmann et al., 2003).

The effects of different effective charges are shown in [Figure 5.1d](#). Note that the charge is only involved in the Coulomb term,

$$U_{Coulomb} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} = \frac{e^2 q_i q_j}{r_{ij}} \quad (2)$$

and does not affect the BMH repulsive term. In equation 2, ϵ_0 is the permittivity of free space and e is the elementary charge, in accordance with Coulomb's law.

Van der Waals coefficients

In addition to the variability in the parameter space of the repulsive term of the potential, there are other possible terms in the potential. The van der Waals terms are the most commonly included and reflect the dipole-dipole and dipole-quadrupole attractions, which are usually written as C_{ij}/r^6 and D_{ij}/r^8 respectively. In most formulations of the potential, D_{ij} is zero, as the contributions are extremely small at interatomic distances relevant to crystals and glasses. The van der Waals coefficients

were initially evaluated by Mayer (1933) and were used without tuning in the work by Fumi & Tosi (1964a). The effects of C_{ij} and D_{ij} parameters on the shape of a cation-anion ionic potential are shown in [Figures 5.3a and 5.3b](#), respectively, and the parameters are reported in Supplementary Table 1.

In some publications, C_{ij} is treated as the product of terms identifiable with each atom type C_i and C_j , while in others, it is an independently tuned parameter for every pair of atoms, similar to the multiple formulations of ρ . Several authors simplify the van der Waals term by setting select cation coefficients to zero (e.g., Na, K, Fe in Guillot & Sator, 2007; Si, Al in Wang et al., 2021) or only considering this attractive force for anion-anion interactions (e.g., Gruenhut et al., 2005; Habasaki 1991). Many others either ignore the van der Waals terms or explicitly set the coefficients to zero, as the contribution from the dispersion terms is considered to be the weakest of intermolecular forces and therefore not worth the computational cost. It is also true that C_{ij} parameters are challenging to constrain by *ab initio* calculations, including the fact that there is a non-zero chance of an unphysical runaway at very short distances, as discussed by Guillot & Sator (2007) and as shown in Figure 3a.

As a result of the non-uniformity of approaches, C_{ij} varies (like A_{ij}) by several orders of magnitude among different authors. For example, C_{Ca-O} is ~ 11 in Huang et al. (2022) while the same parameter is ~ 235 in Matsui (1994) and ~ 980 in Guillot & Sator (2007). The dimension of this parameter is energy times length⁶, or units of kcal/mol * Å⁶ in the preceding cases.

Other terms

Although uncommon, it is possible for authors to include additional terms. One of these is the second nearest-neighbor repulsion, which was used in the original formulation of the BMH equation (Fumi & Tosi; Ida, 1976). Another is the Morse or Pedone potential (Pedone et al., 2006), used to describe the covalent interactions of ions in a system. In some cases, all interactions are described by the BMH equation and select interactions are given Morse terms (e.g., Nozaki et al., 2001; Xu et al., 2013). Akdeniz et al. (1999) included terms to describe the polarization and shell deformation to better describe the behavior of Al-F and Na-F bonds.

Force distance cut-offs

Although they are not considered official parameters of the BMH equation, it is important to note that authors use different force cut-offs for the repulsive and/or Coulombic potentials. The repulsive term of the potential is commonly referred to as the short-range interaction, and as such, many authors set it to have a cut-off several angstroms shorter than the Coulombic term (8 and 12 Å in Bauchy (2014), respectively; 8 and 10 Å in Wang et al., 2020). This approach is not universal, however, and authors may use the same cut-off for both (12 Å in Senyshyn et al., 2005; 20 Å in Ding et al., 2018) or a longer distance for the repulsive term than for the Coulombic term than the repulsive term (10 and 8 Å respectively in Wang et al., 2021).

It is not common for authors to report the distances used, as noted by Bauchy (2014). Computational software packages like LAMMPS do not generally have a default truncation length, so recommended values for this remain poorly known. In one such example, Gruenhut & MacFarlane (1995) suggest using half the length of the box, as this is the largest possible spherical cut-off.

We ran a series of tests to determine the significance of the cut-off ranges for BMH and Coulomb terms. We observe no significant effect of potential cut-off on the bulk simulation properties (i.e., average pressure, internal energy), although slight differences were observed in the exact values at a given time ([Figure 5.5](#), Table 2). Similarly, there were small differences in atomic behavior (e.g., MSD, diffusion; Table 2), but these variations were not substantial. Instead, the effect of different cut-offs most strongly affected the runtime, as shown in Table 2. The optimal conditions for the machine used (maximum timesteps per second) were 6 Å for the BMH potential and 10 Å for the long-range Coulomb potential, but different subprocessors and computing clusters may have other ideal cut-offs, so it is recommended to experiment when performing these computations.

Table 5.2 – Effects of cut-off lengths on simulation metrics

BMH Cut-off (Å)	Coulomb Cut-off (Å)	Time-steps/s	Dominant process (%)	Neighbors per atom	PE (kcal/mol)	$\log_{10}(D_{Si})$ (m ² /s)
5	5	21	Kspace (95)	29	-80488	-7.821
6	12	63	Pair (75)	301	-80483	-7.841

12	12	50	Pair (80)	300	-80516	-7.841
6	10	82	Pair (58)	182	-80497	-7.836
10	10	66	Pair (63)	182	-80492	-7.838
10	8	49	Pair=Kspace (45)	182	-80546	-7.824

Fitting strategies

There are many approaches to the tuning of the force-field parameters. Popular methods include fitting to:

- experimentally observed bond lengths or lattice parameters (i.e., crystallographic *a* or *c* axis)
- *ab initio* calculations of the energy well around the equilibrium volume
- experimentally derived density
- elastic and/or electric constants

Less common methods include fitting Raman band frequencies to observations or matching previously computed pair-correlation functions. Some authors, particularly when investigating multi-component spaces, elect to use multiple types of data, such as dielectric constants and structural parameters (Lewis & Catlow, 1976). Others use previously derived parameters to constrain the fitting of new elements. For example, Nozaki et al. (2001) used previously determined parameters for O, La, and Ti to determine new parameters for K, Na, and Li. A related approach taken by some authors is to fit the parameters in multiple stages. For example, authors first fit cation-anion interaction parameters using *ab initio* calculations, then tailor the coefficients

on cation-cation and anion-anion pairs to other data, such as diffusivities and volumes (Jakse et al., 2021) or pressure (Gruenhut et al., 2005).

There are many considerations to account for when fitting the force-field parameters. First, multi-component spaces will inevitably have multiple viable solutions ([Figure 5.4](#) and Table 3) and additional constraints are usually needed to verify sets of parameters. Second, the parameters fit independently should be similar for identical atoms (i.e., A_{Na-Na} from Na_2O should equal A_{Na-Na} from NaF). Third, in complicated parameter spaces, the best possible fit may not be found if the initial guess is poor, and thus the fit algorithm may require multiple initial guesses (e.g., Monte Carlo) or other fitting approaches if there is little information about the parameter in question. Some approaches are insensitive to certain parameters, as seen in [Figure 5.6](#). As discussed in earlier sections, σ parameters are well constrained and ρ occurs in a small range of values, but A_{ij} vary over several orders of magnitude.

Table 5.3 – Parameters used to create potentials displayed in Figure 5.4

	ρ_{ij} (Å)	σ_{ij} (Å)	A_{ij} (kcal/mol)	C_{ij} (kcal/mol * Å ⁶)	q_{Eff}
a	0.30	2.65	1.0	0	1
b	0.25	2.65	0.55	0	1
c	0.30	2.40	2.40	0	1
d	0.25	2.65	0.40	0	0.8
e	0.28	2.65	1.0	50	1

The number of free parameters varies depending on the assumptions described above. For a binary compound, for example, there will be two σ_i values, one to three ρ values, three A_{ij} values (which may or may not be free), and one degree of freedom in effective charges for a total of five to nine free parameters. When assuming that ρ_{ij} is additive and A_{ij} are independent, this becomes eight variables to fit. In the case of a ternary (e.g., $\text{CaF}_2\text{-CaO}$), there will be three σ_i , three ρ_i , six A_{ij} , and one degree of freedom in effective charges. In the case of the eleven-element system presented here ($\text{Na-K-Ca-Ti-Zr-La-Al-Si-H-O-F}$), there are 11 σ_i and ρ_i values, one degree of freedom in effective charge, and 66 A_{ij} coefficients to determine. However, the mixed cation-cation pre-exponential terms are calculated from averages of their constituent elements, so the number of A_{ij} values to fit decreases to 30.

A summary of references where similar approaches have been adopted, their form of the BMH equation, and the fitting methods applied is presented in Supplementary Table 2.

Computed Properties

Physical Properties

The physical and structural properties are the most commonly targeted outputs in molecular dynamics simulations. This includes bond lengths, bond angles, lattice parameters for crystals, nearest-neighbor or coordination numbers, and density or volume. The structural parameters evaluated through use of the BMH potential are

usually very close to the experimentally observed values, and cases where they are not are generally interpreted to be the result of poorly chosen parameters.

These properties are frequently evaluated through examination of radial distribution functions (RDFs, often symbolized by $g(r)$) and partial distribution functions (PDFs). These functions yield the probability of finding any atom (in the RDF) or an atom of type j (in a PDF) at distance r from an atom of type i (Figure 5.7). The first maximum is the average bond length, and the first minimum beyond the first maximum is considered to define the radius of the first coordination shell. RDFs and PDFs are obtained from simulations by summing all atoms of the respective types over many time steps. Similarly, bond angles are calculated by evaluating the angle between three atoms, usually i - j - i or less frequently i - i - i and i - j - k , over many time steps.

Coordination number (CN) is calculated from the integration of the PDF up to the first minimum beyond the first maximum (Figure 5.7). This is a scalar that constrains the bonding environment of the central atom (i.e., if $CN_{Si} = 4$, then Si is most likely in a tetrahedral site; Bauchy, 2014). An additional structural parameter closely related to CN and bond angle is the calculation of bridging or non-bridging atoms, usually network forming atoms like O. The CN of Si about O will be 1 for a completely depolymerized silicate structure and 2 for a fully polymerized silicate structure (at very high pressure, O triclusters may start to form and the CN of Si about O may exceed 2). The proportion of bridging oxygens may be reported as a percentage or

fraction of the total oxygen atoms, and is an expression of the polymerization of a melt or crystal.

Density and volume are found through NPT calculations, in which the system of a fixed number of atoms (N) is kept at constant pressure (P) at a given temperature (T). These calculations differ from the canonical, or NVT, ensemble, in which the macroscopic properties held constant are the number of atoms, volume, and temperature (Martyna et al., 1994).

Bond lengths are usually in good agreement with previously published MD studies and experimental results, such as X-Ray diffraction (XRD) or neutron diffraction. For example, Na-F bond lengths reported by eight authors ranged from 2.11 to 2.41 Å, compared with experimental values between 2.20 and 2.32 Å. However, this is not the case for all atom pairs. In some papers, authors may interpret that an RDF shows there is no bond while other papers identify a bond length clearly. An obvious example of this is Si-F; Huang et al. (2022) report that these atoms do not bond, but in Sasaki et al. (2003) and Wang et al. (2021) there is a clear bond. A summary of reported cation-anion bond lengths is presented in Supplementary Table 3.

Publications with examples of physical properties can be found in Supplementary Table 4.

Transport Properties

Another popular motivation to run a simulation with BMH potentials is to evaluate the transport properties of a glass or melt under conditions not easily attained in experimental work (de Koker & Stixrude, 2010). These properties primarily include self-diffusivities (D_i) and shear viscosities. Generally, diffusivities are determined through plots of mean-squared displacement (MSD). The slope of MSD versus time yields the diffusion coefficient, following the Einstein relation: $D_i = \text{MSD}/6t$ for a three-dimensional simulation. Less commonly, the diffusion of a species may be determined through the Green-Kubo formulation of the normalized velocity autocorrelation function (e.g., Ciccotti et al., 1975),

$$D_i = \frac{k_B T}{m_i} \int_0^\infty \langle v_i(0)v_i(t) \rangle / \langle |v_i|^2 \rangle dt \quad (3)$$

Although this equation should converge at very long timescales, the length is beyond the scope of many simulations, especially ab initio simulations.

Viscosity (η) can be calculated multiple ways (Hess, 2002). A common way involves using a normal, well-equilibrated simulation and the Stokes-Einstein-Sutherland, or simply Stokes-Einstein, equation: $\eta = k_B T / 2\pi D_i r_i$. In some cases, r_i is assumed to be the jump distance r_0 for all elements (e.g., Du et al., 2022), while others use r_i to refer to the ionic radius of a specific element. The advantage of this approach is that it can be easily calculated from any molecular dynamics run. However, the differences in ion behavior due to charges, abundance, and macrostructure in melt (i.e., network or bridging sites) and the requirement of low Reynolds number mean

that viscosities calculated this way are not always accurate. Another equilibrium approach utilizes the Green-Kubo formula,

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xz}(t_0) P_{xz}(t_0 + t) \rangle dt \quad (4)$$

which takes the autocorrelation of the off-diagonal terms of the stress tensor. As with diffusion, the autocorrelation function of stress will eventually converge, but the time it takes to do so is not feasible for most ab initio calculations (e.g., Ding et al., 2018).

Other methods for evaluating viscosity arise from non-equilibrium simulations that directly apply a shear strain rate to the system and extract the resulting shear stress (Hess, 2002). These are also simple to set up (e.g., Delaye & Ghaleb 1996; Johnson et al., 2022), although authors generally do not perform these runs unless viscosity is the primary focus of the paper, such as Ciccotti et al. (1975) or Ding et al. (2018).

Examples of publications with calculated transport properties are indicated in Supplementary Table 4. A summary of calculated diffusion coefficients and viscosities are presented in Supplementary Table 5 and compared to experimental values collected by Zhang et al. (2010).

Elastic Properties

Elastic properties include the elastic constants or stiffness tensor (c_{ij}) and elastic moduli such as the shear modulus (μ), the bulk modulus (KT or KS, the inverse of compressibility), the Young's modulus I , and the Poisson ratio (ν). These values,

particularly the bulk and shear moduli, are important to geoscience, notably in seismology. Publications by Matsui (1994, 1996b), Guillot & Sator (2007), and others suggest that the BMH equation can be used to accurately compute some of these properties, especially K . However, other studies by Bauchy (2014) and Sangster and Dixon (1976) indicate that the estimated values are not always to be trusted.

Electronic Properties

Electronic properties that can be calculated through molecular dynamics include conductivities, ion polarizabilities, and dielectric constants. However, the free-ion polarizabilities and dielectric constants are more frequently used as input to tune the BMH parameters rather than as outputs to be predicted. Pioneering work on this topic was done by Sangster & Dixon (1976), who focused on fitting alkali halide potentials to these electronic constants, followed by Lewis & Catlow (1985), who computed potentials using a combination of structural and electronic properties. It is possible to calculate the dielectric constant as an unknown (e.g., Senyshyn et al., 2005), though this is uncommon. Similarly to viscosity, there are multiple ways to calculate the electrical conductivity of a melt or glass. One way involves the Green-Kubo formulation of the electrical current auto-correlation function (e.g., Ciccotti et al., 1975) and another is through the Nernst-Einstein relation, relating conductivity to diffusivity (e.g., Guillot & Sator, 2007).

Thermal Properties

There are several thermal properties that can be evaluated with simulations run with the BMH potential, including the thermal conductivity (a transport property), heat capacity, and thermal expansion coefficient. The thermal conductivity of a simulation can be found with equilibrium (e.g., Green-Kubo autocorrelation of the heat flux; Huang et al., 2022; Rittirum et al., 2016) or non-equilibrium methods (ratio of heat flux or kinetic energy to a temperature gradient; Ding et al. 2018; Wei et al., 2022). The intensive specific heat capacity at constant volume (c_V) or pressure (c_P), or extensive heat capacity (CV and C_p) are relatively simple to calculate from a given NVT or NPT simulation, respectively (Wei et al., 2022; Guillot & Sator, 2007). The most commonly reported method is to take the temperature derivative of enthalpy at constant pressure ($C_p = (\partial H / \partial T)_P$). The thermal expansion coefficient (α) is less frequently reported but can be calculated from the derivative of volume with respect to temperature at constant pressure (e.g., Guillot & Sator 2007; Senyshyn et al., 2005).

Vibrational/Optical Properties

It is also possible to compute several vibrational or optical properties with molecular dynamics, but classical potentials, including the BMH potential, are not generally the most accurate method (Bauchy, 2014). The most important of these properties are the vibrational density of states (VDOS) and the phonon density of states (PDOS), found through a Fourier-transform of the velocity autocorrelation function, and generally compared to neutron measurements (e.g., Bauchy, 2014; Senyshyn et al.,

2005; Huang et al., 2022; Sangster, Takahashi). Vibrational modes can also be computed for comparison to experimental infrared and Raman spectra (e.g., Akdeniz et al., 1999; Kawamoto et al., 1985; Nozaki et al., 2001), as well as frequencies of fluorescence (Shojiya et al., 1999).

Concluding remarks

The increase in computational accessibility has diversified both the definitions and the form of the Born-Mayer-Huggins interatomic potential, with a significant number of customizable approaches, some of which are mutually incompatible. This unfortunately means that the field may be daunting for those new to using force fields. The best approach is to identify previous works that investigated similar elements and determined whether the assumptions used in the parameter fitting are appropriate for the work at hand. Then, any elements not included in the previous publications should be fit using the same approach. It is not recommended to pick elements from different publications without consideration.

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Figures

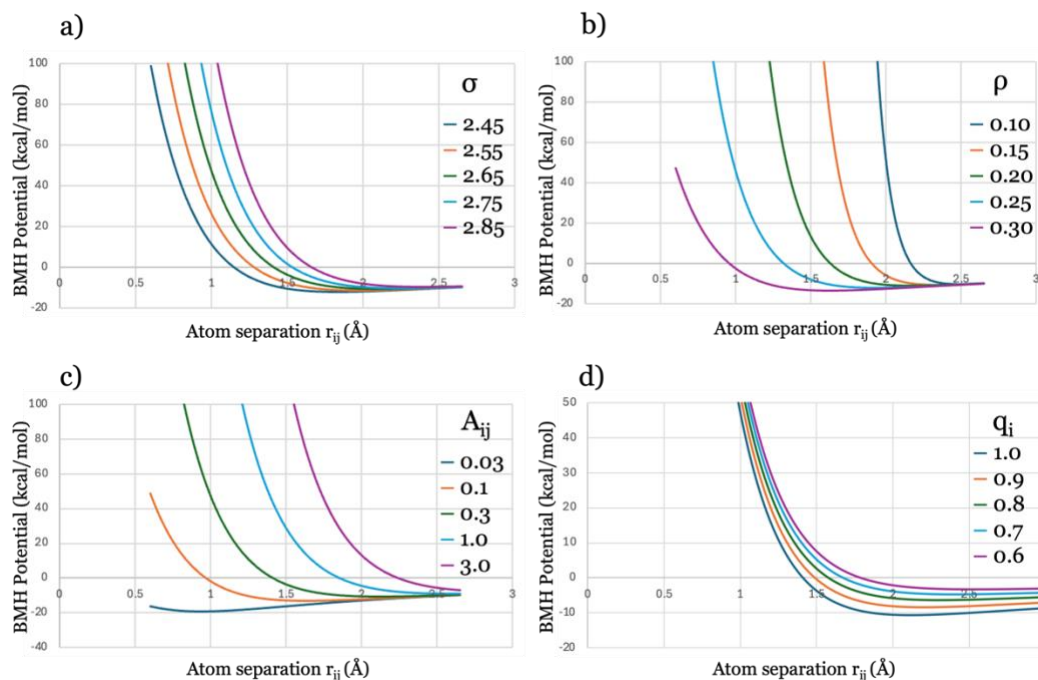


Figure 5.1 – The BMH potential parameters.

The effects of BMH parameters on the shape and placement of the interatomic potential. The parameters are the characteristic separation ([a](#), Å units), the hardness parameter ([b](#), Å units), the pre-exponential ([c](#), kcal/mol units), and the effective charge ([d](#), the fraction of the nominal charge) of the atom pair (i.e., $\sigma = \sigma_i + \sigma_j$). The different ranges in displayed parameters (i.e., 2.45-2.85 Å in σ and 0.03-3.0 kcal/mol in A_{ij}) reflect the variety of values published in the literature.

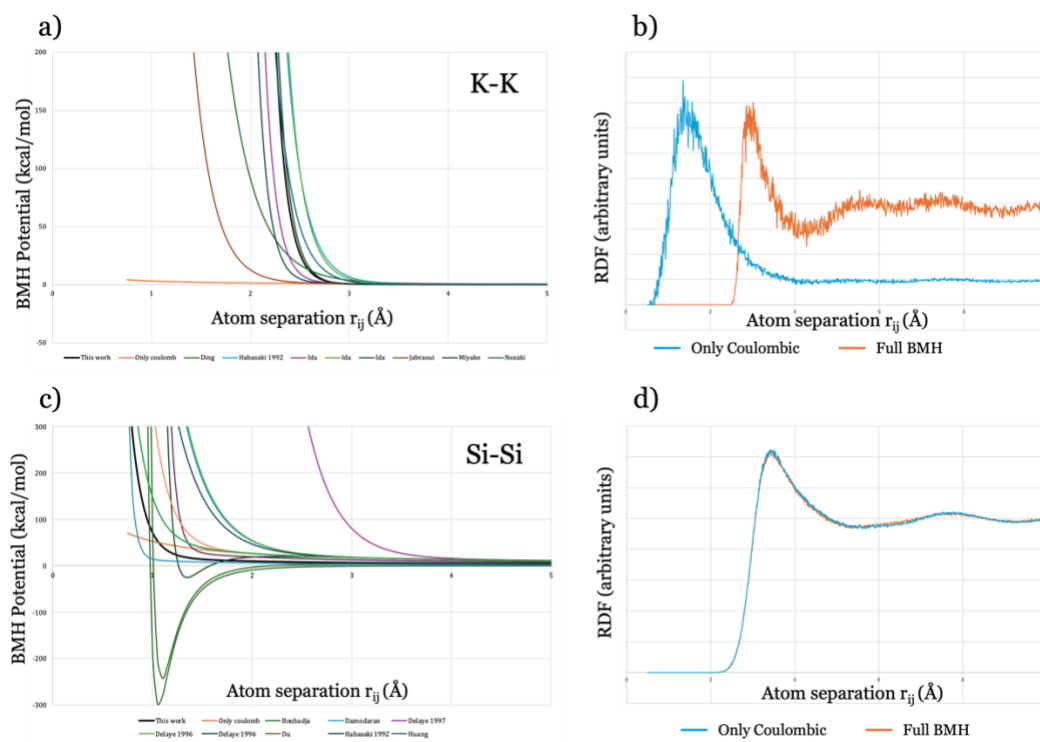
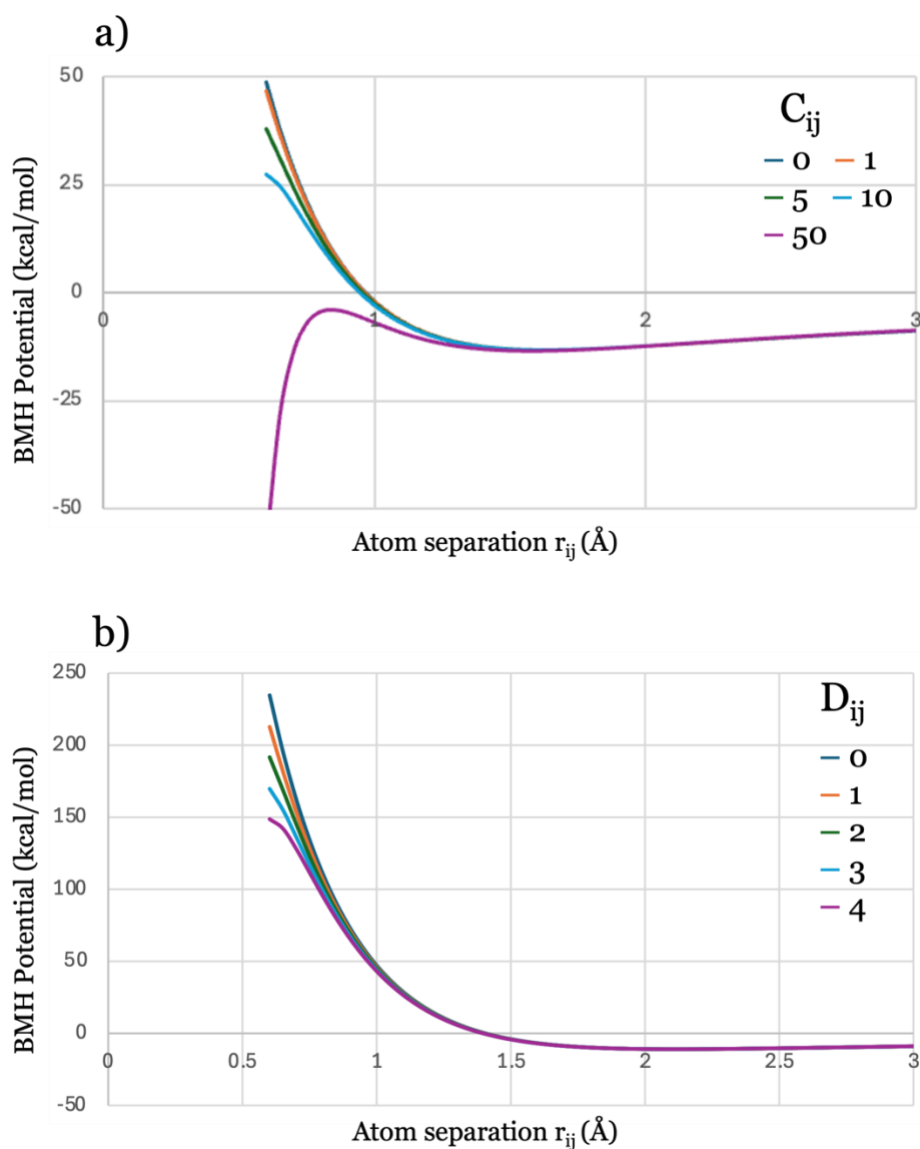


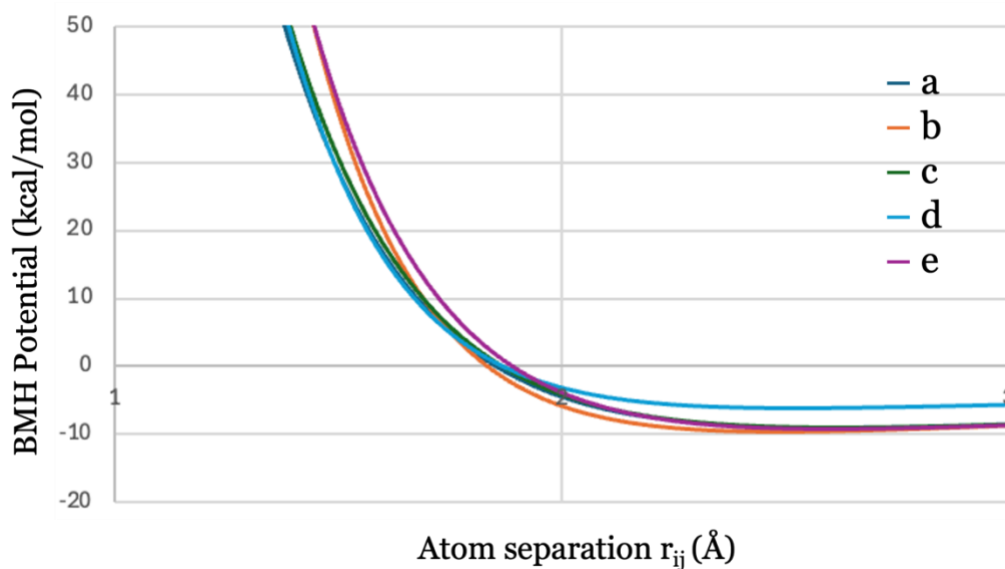
Figure 5.2 – Coulombic potential with and without BMH terms

The effects of relying on only the Coulombic term of the interatomic potential for two cations, showing the poor results for a low-charge ion (K, 2a & 2b) and the acceptable results for a high-charge ion (Si, 2c & 2d). In both cases, the potentials built with only a Coulombic interaction are much less repulsive at small separation than potentials that include the BMH term (2a & 2c). The result of this is exacerbated in ions with low charges like K^+ , resulting in a radial distribution with a peak at much closer distances (2b). The difference in peak position is negligible with ions like Si^{4+} (2d).



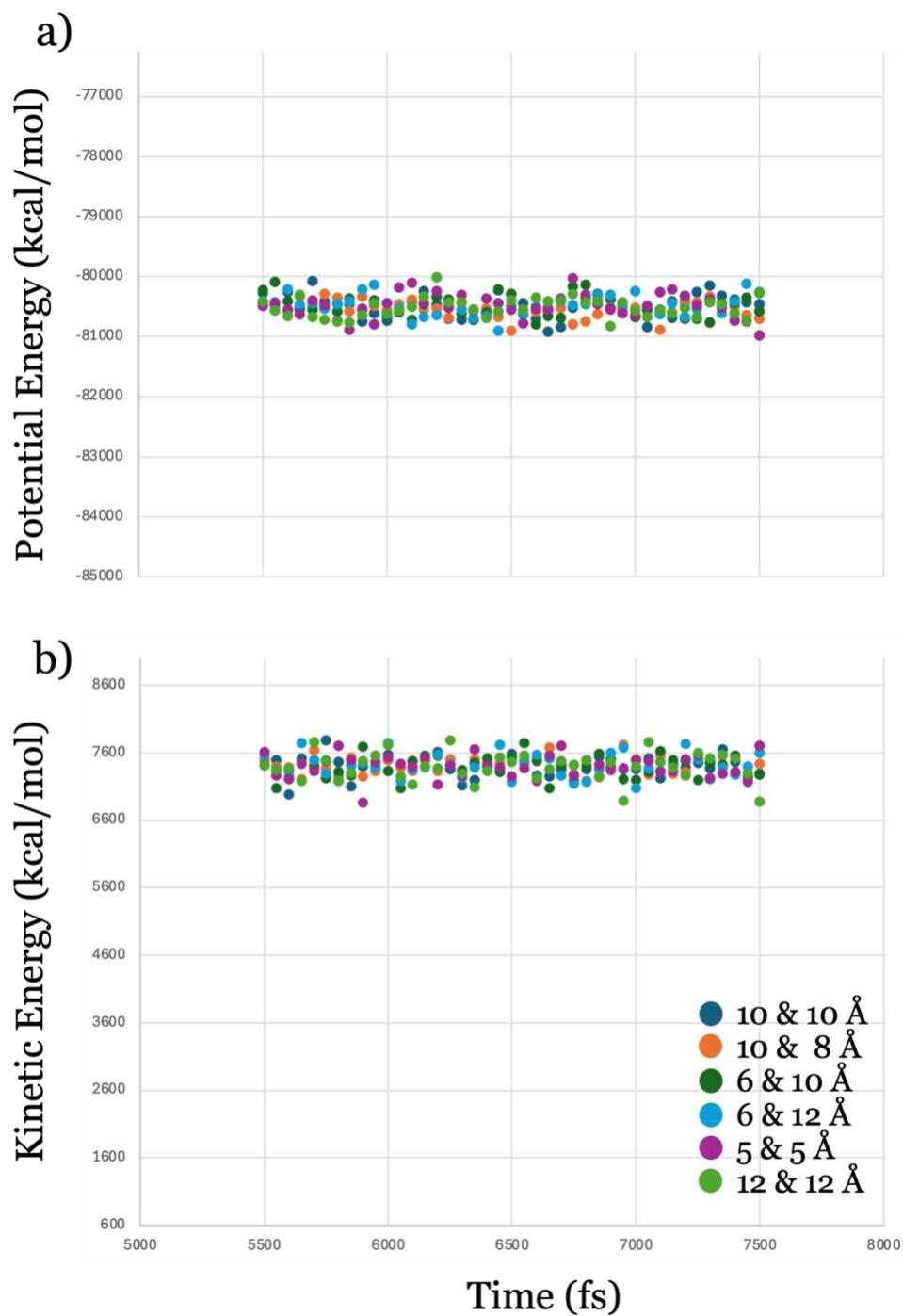
[Figure 5.3](#) – Van der Waals terms of the BMH equation

The effects of the Van der Waals coefficients on the shape and placement of the interatomic potential. The parameters are the dipole-dipole attraction (a, kcal/mol/Å⁶ units) and the dipole-quadrupole attraction (b, kcal/mol/Å⁸ units) for the atom pair. The ranges in displayed parameters (i.e., 0 – 50.0 kcal/mol/Å⁶ in C_{ij}) reflect the variety of values published in the literature.



[Figure 5.4](#) – Multiple solutions to a BMH fit.

A demonstration of the non-uniqueness of solutions to the BMH equation, as presented in Table 3. There are many possible combinations of parameter values that result in similar potentials, so simply fitting the parameters to an assumed potential is not an effective method to find accurate values and instead, should be used when combined with other approaches like fitting to ab initio quantities (e.g., equilibrium energy) or experimentally derived properties (e.g., density).



[Figure 5.5](#) – Force-field cut-off distances

The effects (or lack thereof) of different force-field cut-offs on simulation properties, including the potential energy (a) and the kinetic energy (b). The key displays the

cut-offs used for the repulsive (BMH) and Coulombic terms of the potential. There is no effect on the actual computed properties during a simulation, although there are differences in the economy of the simulation (Table 2), where longer cut-offs result in more neighbors-per-atom and shorter ones require more energy spent on the Kspace calculations. There is no community consensus on whether the BMH term or the Coulombic term should be longer, or if they should be the same.

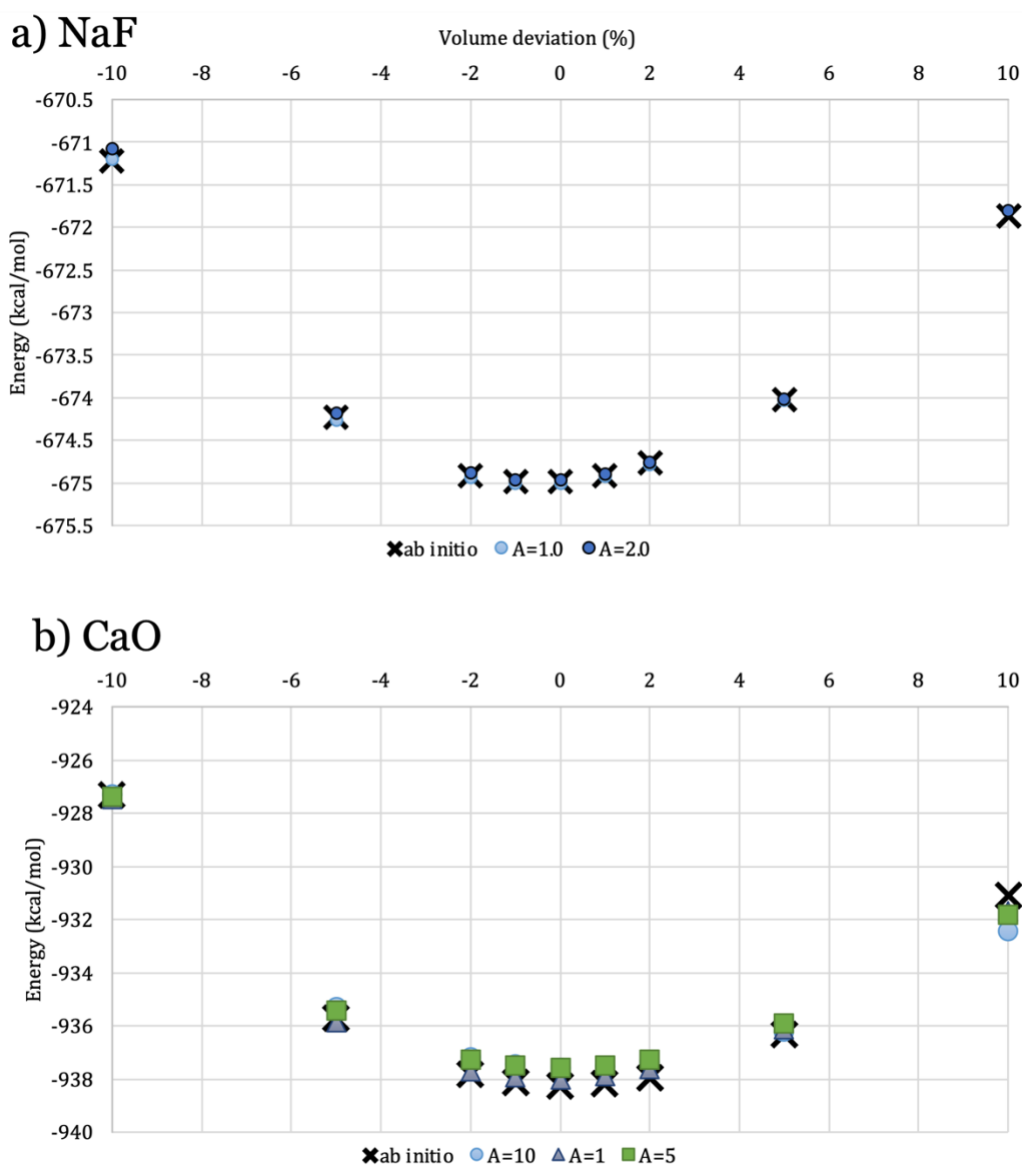
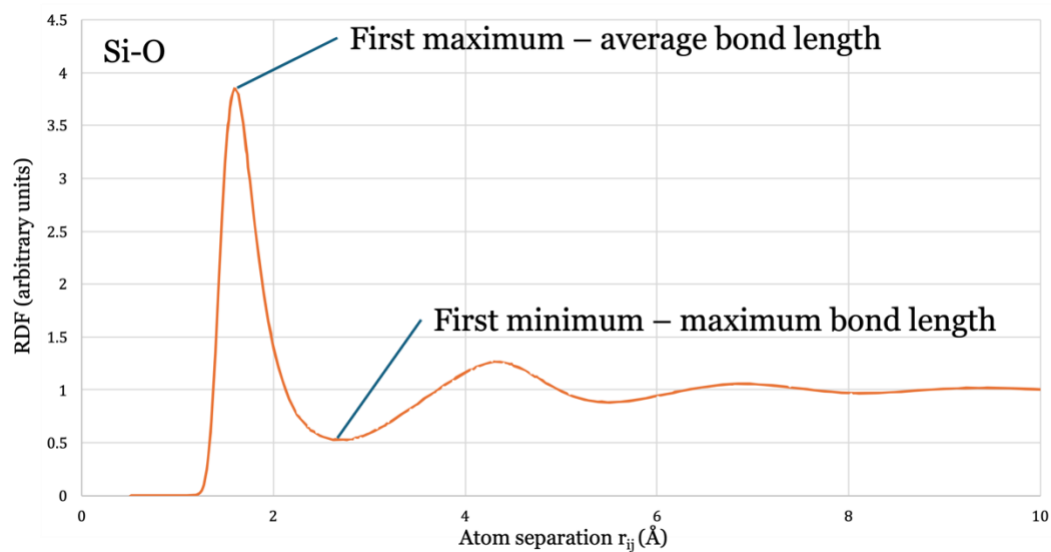


Figure 5.6 – Ab initio and force-field energy comparison.

Examples of internal energy fitting for two binary compounds, NaF (a) and CaO (b), showing the *ab initio* calculated energies at equilibrium volume and $\pm 1, 2, 5$, and 10 % volume deviations (x marker). Both fittings also show the effects of the cation-cation ($A_{\text{Na-Na}}$ and $A_{\text{Ca-Ca}}$) pre-exponential variable of the potential, and how insensitive the internal energy calculation is to this parameter.



[Figure 5.7](#) – Labelled RDF

An example partial radial distribution function (RDF), including Si and O, labelled to show the first peak and first minimum, which indicate the average and maximum bond lengths, respectively.

Appendix

Supplementary Files in Deposit:

S. Table 1 – Compiled values

S. Table 2 - Forms of the interatomic potential, omitting Coulomb term.

For ease of legibility, all equations have been given the same notation and similar assumptions/forms of the equation have been colored.

$$U = \text{Repulsive term} \quad \text{Van der Waals attractive term(s)}$$

$$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$$

Legend

A_{ij}, B_{ij} = pre-exponential constant

In this table: $B_{ij} = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j}{\rho_{ij}}\right]$

- units of energy per count (kcal/mol)

C_{ij}, D_{ij} = Van der Waals constants

- units of energy per count*length⁶ or energy per count*length⁸, respectively

σ_i = characteristic radius of ion i, sometimes “ q_i ” or “ a_i ” in text

- units of length (Å)

ρ_i = hardness factor of ion i, sometimes “ p_i ” or “ b_i ” in text

- units of length (Å)

$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}$; Pauling factor

- unitless

Z_i = nominal charge of ion i

n_i = number of valence-shell electrons of ion i (generally 8)

b = universal constant, sometimes a fit parameter

- units of energy (kcal/mol or erg) or energy/molecule, not always specified

f_0 = unit conversion constant, sometimes a fit parameter

- units of energy per count/length or force (kcal/(Å*mol) or N), not always specified

Table 2a - References, sorted by form of equation

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Constant in front of exponent is fit to data					
Bauchy, 2014	O, Al, Si, Ca	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters from Matsui 1996a; Bouhadja et al., 2013; Delaye et al., 2001	BMH fit	12/8
Bouhadja and Jakse, 2021	O, Al, Si, Ca	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to structures derived from <i>ab initio</i> calculations	BMH fit	
Jakse et al., 2021	O, Al, Ca, Ti	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit by matching pair-correlation functions from <i>ab initio</i> calculations	Coulomb	
Alderman et al., 2014	O, Ti	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} + U_{Morse}$	Parameters from Matsui 1991	BMH fit	12/ unstated
Ding et al., 2018	O, Na, K, (C)	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	All parameters from Tissen & Janssen, 1993	BMH fit	20/20
Kilner and Brook, 1982	O, Al, La, (Ln)	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Al, O parameters from James 1979; Ln parameters from lattice dielectric constants	Coulomb	
Lucas et al., 1984	F, Zr, (Ba)	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Parameters fit to structure data and density	BMH fit	
Chen et al., 2021	F, Na, Al, K	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match zero-point energy	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Du et al., 2022	O, F, Si, Ca, (P)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters from Fan et al 2015; Belashchenko et al 2002; Hirao & Kawamura 1994	BMH fit	Unstated/ 10
Gruenhut and Macfarlane, 1995	F, Zr, (Li, Ba)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters recalculated from Ciccotti et al. 1976; Lucas et al. 1984	BMH fit	Unstated/ 7.38
Guillot and Sator, 2007	O, Na, Al, Si, K, Ca, Ti, (Mg, Fe ³⁺ , Fe ²⁺)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match density of materials at zero pressure	Coulomb	10-11/ Unstated
Lewis and Catlow, 1985	O, Al, Ca, Ti, Zr, (many)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match unit cell or elastic & electric constants	Coulomb	
Senyshyn et al., 2005	O, La, (Ln)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	O-O parameters from Lewis & Catlow, 1985; La-O parameters fit to match zero-point energy	Coulomb	12/12
Wang et al., 2019	O, F, Al, Si, Ca	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters from Delaye et al 1997; Shimoda & Saito 2007; Miyake 1998 Potential typo in table (V -> eV?)	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Belashchenko et al., 1998	F, O, Na, Al, Ca	$U = B_{ij} \exp\left[\frac{-r}{\rho_0}\right]$	Parameters from previous works by same authors, fit by matching molar volume	Coulomb	
Delaye et al., 1997	O, Na, Al, Si, Zr, (B)	$U = B_{ij} \exp\left[\frac{-r}{\rho_0}\right]$	Parameters from Delaye and Ghaleb, 1996	BMH fit	
Constant in front of exponent is Pauling factor times some constant					
Boswarva, 1981	F, Na, K, (Li, Cl, Br, Rb, I)	$U = 6b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{\text{rel}}}\right] + U_{\text{secondary}}$	One set of new data (unclear fitting method) and citations from Fumi & Tosi, 1964; Mayer 1933	BMH fit	
Busing, 1972	F, (Li, Be)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Fumi & Tosi, 1964	BMH fit	
Ciccotti et al., 1976	F, Na, K, (Li, Cl, Rb, I)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{\text{rel}}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters from Fumi & Tosi, 1964	BMH fit	
Damodoran et al., 1990	O, Si, Zr	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Unclear	BMH fit	
Delaye and Ghaleb, 1996	O, Na, Si, Zr, (B)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Na, Zr parameters fit (?); O, Si parameters from Kiefer & Angell 1989	BMH fit	13/6.5

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Fumi & Tosi, 1964; Tosi & Fumi, 1964	F, Na, K, (Li, Cl, Br, Rb, I)	$U = 6b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{xcl}}\right] + U_{secondary}$ $U_{secondary} = \frac{C_{ij}}{r^m} - \frac{D_{ij}}{r^n}$	Parameters fit to energy and experimentally derived properties	BMH fit	
Gruenhut et al., 2005	F, Na, Zr, (Ba)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^m} - \frac{D_{ij}}{r^n}$	Parameters from Gruenhut & Macfarlane 1995	BMH fit	
Janssen and Tissen, 1990	O, Na, K, (Li, C)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] + U_{secondary}$	Parameters fit to short-range ab initio energy	BMH fit	
Kawamoto et al., 1985	F, Zr, (Ba, Eu)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	F parameters from Fumi & Tosi, 1964; others fit to bond lengths	BMH fit	
Parker, 1987	F, Na, Al, Zr, (Li, Ba)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Parameters from Angell et al 1982; Lucas et al 1984; Hamill & Parker 1985; Kawamoto et al 1985	BMH fit	
Sangster, 1976; Sangster et al., 1978	F, Na, K, (Li, Cl, Br, Rb, I)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j}{\rho_{xcl}}\right] * \exp\left[\frac{-r}{\rho_{xcl}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters fit to match dielectric constant, optic frequency, polarizabilities	BMH fit	
Wei et al., 2022	Ca, (Cl)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from multiple sources	BMH fit	20/20
Woodcock et al., 1976	O, Si, K, (Be, Cl, Zn)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Parameters fit to pair distribution functions	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
<i>Constant in front of exponent is rho times some constant</i>					
Hendy and Edgar, 2006	F, Na, Al, Zr, La, (Cl, Ba)	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Na, La parameters fit to match lattice constant; F, Zr parameters from Takahashi et al 1995	BMH fit	
Sasaki et al., 2003	O, F, Na, Si	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters from Hirao & Kawamura 1994	BMH fit	
Shojiya et al., 1999	F, Na, Al, Ca, (Cl, Cd, Ba, Eu)	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters fit to match MD of binary halides	BMH fit	
Suzuki et al., 1998	O, Zr, (Y, Ce)	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters fit to match lattice constant and thermal expansion coefficient	BMH fit	
Takahashi et al., 1995	F, Zr, (Cl, Ba, Eu)	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters fit to match structure	BMH fit	
Xu et al., 2013	O, Zr, (Y)	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters from previous work by authors, fit to match lattice constant and thermal expansion coefficient	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Akdeniz et al., 1999	F, Na, Al	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{polarization} + U_{shell}$	Al, Na parameters fit to match bond length; F parameters from Li & Tosi 1988	BMH fit	
Habasaki, 1991	O, Si, (Li)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match XRD interference functions	BMH fit	
Habasaki and Okada, 1992	O, Na, Si, K, (Li)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Si, O parameters from Tsuneyuki et al., 1989; others fit to ab initio energy	BMH fit	
Hauptmann et al., 2003	H, O, F, Ca, (P)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to optical data	BMH fit	13
Huang et al., 2022	O, F, Si, Ca	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Sangster & Dixon, 1976	BMH fit	8/10
Jabraoui et al., 2016	O, Na, Si, K, (Li)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters from Habasaki and Okada, 1992	BMH fit	12/8
Matsui, 1994	O, Al, Si, Ca, (Mg)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match structure	BMH fit	
Miyake, 1998	O, Na, Al, Si, K, Ca, (Mg)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{Morse}$	Parameters fit to structural data	BMH fit	
Wang et al., 2020	O, Na, Al, Si, Ca, (Mg)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Matsui 1994-1996	BMH fit	10/8

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Wang et al., 2021	O, F, Na, Al, Si, Ca	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Hirao & Kawamura 1994	BMH fit	8/10
Zhao et al., 1995	F, (Li, Ba, Th)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters "determined experimentally"	BMH fit	
Constant in front of exponent is mixed Pauling/fit/rho terms					
Ida, 1976	F, Na, K, (Li, Cl, Br, Rb, I)	$U = \beta_{i,j} f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] + U_{secondary}$	Parameters fit to match zero-pressure electrostatics	BMH fit	
Nozaki et al., 2001	O, Na, K, Ti, La, (Li)	$U = \beta_{i,j} f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{Morse}$	K, La, Na parameters fit to match Raman band frequencies; O, Ti parameters from Hirao & Kawamura 1994	BMH fit	
Rittiruam et al., 2016	O, Ti, La, (Sm, Er)	$U = \beta_{i,j} f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{Morse}$	Parameters from Ida 1976; Vora-ud et al. 2016	BMH fit	
Shanker and Agrawal, 1980	F, Na, K, Ca, (Li, Cl, Br, Rb, Sr, Ag, Cs, Ba, H)	$U = b * \beta_{i,j} (\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} + b * (\beta_{i,j} \exp\left[\frac{2\sigma_i - \sqrt{2}r}{\rho_{ij}}\right] - \beta_{j,j} \exp\left[\frac{2\sigma_j - \sqrt{2}r}{\rho_{ij}}\right])$	Parameters fit to match "overlap integrals"	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Soules, 1979	O, Si, Na, K, Ca, (B)	$U = b * \beta_{ij} B_{ij} \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] + U_{Coulomb-Ewald}$	O, Si parameters from Woodcock et al, 1976; others fit to bond length	BMH fit	

Table 2b - References, sorted by author name

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Akdeniz et al., 1999	F, Na, Al	$U = f(\rho_i + \rho_j) \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$ $+ U_{\text{polarization}} + U_{\text{shell}}$	Al, Na parameters fit to match bond length; F parameters from Li & Tosi 1988	BMH fit	
Alderman et al., 2014	O, Ti	$U = A_{ij} \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} + U_{\text{Morse}}$	Parameters from Matsui 1991	BMH fit	12/ unstated
Bauchy, 2014	O, Al, Si, Ca	$U = A_{ij} \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters from Matsui 1996a; Bouhadja et al., 2013; Delaye et al., 2001	BMH fit	12/8
Belashchenko et al., 1998	F, O, Na, Al, Ca	$U = B_{ij} \exp\left[-\frac{r}{\rho_0}\right]$	Parameters from previous works by same authors, fit by matching molar volume	Coulomb	
Boswarva, 1981	F, Na, K, (Li, Cl, Br, Rb, I)	$U = 6b * \beta_{ij} \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_{\text{trial}}}\right] + U_{\text{secondary}}$	One set of new data (unclear fitting method) and citations from Fumi & Tosi, 1964; Mayer 1933	BMH fit	
Bouhadja and Jakse, 2021	O, Al, Si, Ca	$U = A_{ij} \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to structures derived from <i>ab initio</i> calculations	BMH fit	
Busing, 1972	F, (Li, Be)	$U = b * \beta_{ij} \exp\left[-\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Fumi & Tosi, 1964	BMH fit	
Chen et al., 2021	F, Na, Al, K	$U = B_{ij} \exp\left[-\frac{r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match zero-point energy	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Ciccotti et al., 1976	F, Na, K, (Li, Cl, Rb, I)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{xrel}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters from Fumi & Tosi, 1964	BMH fit	
Damodoran et al., 1990	O, Si, Zr	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Unclear	BMH fit	
Delaye and Ghaleb, 1996	O, Na, Si, Zr, (B)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Na, Zr parameters fit (?); O, Si parameters from Kiefer & Angell 1989	BMH fit	13/6.5
Delaye et al., 1997	O, Na, Al, Si, Zr, (B)	$U = B_{ij} \exp\left[\frac{-r}{\rho_0}\right]$	Parameters from Delaye and Ghaleb, 1996	BMH fit	
Ding et al., 2018	O, Na, K, (C)	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	All parameters from Tissen & Janssen, 1993	BMH fit	20/20
Du et al., 2022	O, F, Si, Ca, (P)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters from Fan et al 2015; Belashchenko et al 2002; Hirao & Kawamura 1994	BMH fit	Unstated/ 10
Fumi & Tosi, 1964; Tosi & Fumi, 1964	F, Na, K, (Li, Cl, Br, Rb, I)	$U = 6b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{xrel}}\right] + U_{secondary}$	Parameters fit to energy and experimentally derived properties	BMH fit	
Gruenhub and Macfarlane, 1995	F, Zr, (Li, Ba)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters recalculated from Ciccotti et al. 1976; Lucas et al. 1984	BMH fit	Unstated/ 7.38

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Gruenhut et al., 2005	F, Na, Zr, (Ba)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] - \frac{C_{ij}}{r^m} - \frac{D_{ij}}{r^n}$	Parameters from Gruenhut & Macfarlane 1995	BMH fit	
Guillot and Sator, 2007	O, Na, Al, Si, K, Ca, Ti, (Mg, Fe ³⁺ , Fe ²⁺)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^\delta}$	Parameters fit to match density of materials at zero pressure	Coulomb	10-11/ Unstated
Habasaki and Okada, 1992	O, Na, Si, K, (Li)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^\delta}$	Si, O parameters from Tsuneyuki et al., 1989; others fit to ab initio energy	BMH fit	
Habasaki, 1991	O, Si, (Li)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^\delta}$	Parameters fit to match XRD interference functions	BMH fit	
Hauptmann et al., 2003	H, O, F, Ca, (P)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^\delta}$	Parameters fit to optical data	BMH fit	13
Hendy and Edgar, 2006	F, Na, Al, Zr, La, (Cl, Ba)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Na, La parameters fit to match lattice constant; F, Zr parameters from Takahashi et al 1995	BMH fit	
Huang et al., 2022	O, F, Si, Ca	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^\delta}$	Parameters from Sangster & Dixon, 1976	BMH fit	8/10
Ida, 1976	F, Na, K, (Li, Cl, Br, Rb, I)	$U = \beta_{ij} f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] + U_{secondary}$	Parameters fit to match zero-pressure electrostatics	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Jabraoui et al., 2016	O, Na, Si, K, (Li)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters from Habasaki and Okada, 1992	BMH fit	12/8
Jakse et al., 2021	O, Al, Ca, Ti	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit by matching pair-correlation functions from <i>ab initio</i> calculations	Coulomb	
Janssen and Tissen, 1990	O, Na, K, (Li, C)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right] + U_{secondary}$	Parameters fit to short-range <i>ab initio</i> energy	BMH fit	
Kawamoto et al., 1985	F, Zr, (Ba, Eu)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	F parameters from Fumi & Tosi, 1964; others fit to bond lengths	BMH fit	
Kilner and Brook, 1982	O, Al, La, (Ln)	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Al, O parameters from James 1979; Ln parameters from lattice dielectric constants	Coulomb	
Lewis and Catlow, 1985	O, Al, Ca, Ti, Zr, (many)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match unit cell or elastic & electric constants	Coulomb	
Lucas et al., 1984	F, Zr, (Ba)	$U = A_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Parameters fit to structure data and density	BMH fit	
Matsui, 1994	O, Al, Si, Ca, (Mg)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters fit to match structure	BMH fit	

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Miyake, 1998	O, Na, Al, Si, K, Ca, (Mg)	$U = f(\rho_l + \rho_j) \exp\left[\frac{\sigma_l + \sigma_j - r}{\rho_l + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{Morse}$	Parameters fit to structural data	BMH fit	
Nozaki et al., 2001	O, Na, K, Ti, La, (Li)	$U = \beta_{ij} f(\rho_l + \rho_j) \exp\left[\frac{\sigma_l + \sigma_j - r}{\rho_l + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{Morse}$	K, La, Na parameters fit to match Raman band frequencies; O, Ti parameters from Hirao & Kawamura 1994	BMH fit	
Parker, 1987	F, Na, Al, Zr, (Li, Ba)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_l + \sigma_j - r}{\rho_0}\right]$	Parameters from Angell et al 1982; Lucas et al 1984; Hamill & Parker 1985; Kawamoto et al 1985	BMH fit	
Rittiruam et al., 2016	O, Ti, La, (Sm, Er)	$U = \beta_{ij} f(\rho_l + \rho_j) \exp\left[\frac{\sigma_l + \sigma_j - r}{\rho_l + \rho_j}\right] - \frac{C_{ij}}{r^6} + U_{Morse}$	Parameters from Ida 1976; Vora-ud et al. 2016	BMH fit	
Sangster, 1976; Sangster et al., 1978	F, Na, K, (Li, Cl, Br, Rb, I)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_l + \sigma_j}{\rho_{xtal}}\right] * \exp\left[\frac{-r}{\rho_{xtal}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$	Parameters fit to match dielectric constant, optic frequency, polarizabilities	BMH fit	
Sasaki et al., 2003	O, F, Na, Si	$U = f(\rho_l + \rho_j) \exp\left[\frac{\sigma_l + \sigma_j - r}{\rho_l + \rho_j}\right]$	Parameters from Hirao & Kawamura 1994	BMH fit	
Senyshyn et al., 2005	O, La, (Ln)	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	O-O parameters from Lewis & Catlow, 1985; La-O parameters fit to match zero-point energy	Coulomb	12/12

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Shanker and Agrawal, 1980	F, Na, K, Ca, (Li, Cl, Br, Rb, Sr, Ag, Cs, Ba, H)	$U = b * \beta_{ij} (\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} + b * (\beta_{ii} \exp\left[\frac{2\sigma_i - \sqrt{2}r}{\rho_{ii}}\right] - \beta_{jj} \exp\left[\frac{2\sigma_j - \sqrt{2}r}{\rho_{jj}}\right])$	Parameters fit to match "overlap integrals"	BMH fit	
Shojiya et al., 1999	F, Na, Al, Ca, (Cl, Cd, Ba, Eu)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters fit to match MD of binary halides	BMH fit	
Soules, 1979	O, Si, Na, K, Ca, (B)	$U = b * \beta_{ij} B_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] + U_{Coulomb-Ewald}$	O, Si parameters from Woodcock et al., 1976; others fit to bond length	BMH fit	
Suzuki et al., 1998	O, Zr, (Y, Ce)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters fit to match lattice constant and thermal expansion coefficient	BMH fit	
Takahashi et al., 1995	F, Zr, (Cl, Ba, Eu)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters fit to match structure	BMH fit	
Wang et al., 2019	O, F, Al, Si, Ca	$U = B_{ij} \exp\left[\frac{-r}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6}$	Parameters from Delaye et al 1997; Shimoda & Saito 2007; Miyake 1998 Potential typo in table (V -> eV?)	BMH fit	
Wang et al., 2020	O, Na, Al, Si, Ca, (Mg)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Matsui 1994-1996	BMH fit	10/8

Authors	Elements	Form	Parameters fit or from citation?	Cation-cation treatment	Coulomb/ BMH Cut-off (Å)
Wang et al., 2021	O, F, Na, Al, Si, Ca	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from Hirao & Kawamura 1994	BMH fit	8/10
Wei et al., 2022	Ca, (Cl)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters from multiple sources	BMH fit	20/20
Woodcock et al., 1976	O, Si, K, (Be, Cl, Zn)	$U = b * \beta_{ij} \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_0}\right]$	Parameters fit to pair distribution functions	BMH fit	
Xu et al., 2013	O, Zr, (Y)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right]$	Parameters from previous work by authors, fit to match lattice constant and thermal expansion coefficient	BMH fit	
Zhao et al., 1995	F, (Li, Ba, Th)	$U = f(\rho_i + \rho_j) \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho_i + \rho_j}\right] - \frac{C_{ij}}{r^6}$	Parameters "determined experimentally"	BMH fit	

CHAPTER VI

FLUORINE SPECIATION IN SILICATE MELTS AS
DETERMINED BY MOLECULAR DYNAMICS

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Abstract

Molecular dynamics simulations are a useful tool to investigate the speciation of atoms in silicate melts. However, in order to run them on a geologically relevant scale (both in simulation size and time scale), it is necessary to use force-fields instead of limited, but accurate, *ab initio* calculations. This work presents the force fields of 11 different elements, which include both trace (H, Ti, Zr, La) and major (Al, Ca, Na, K, Si) cations as fluoride, oxide, and oxyfluoride species. The force fields were trained on small-scale, *ab initio* energy-volume calculations performed in the Vienna Ab-Initio Simulation Package (VASP) to calibrate a Born-Mayer-Huggins force field for large-scale simulations (Large-scale Atomic/Molecular Massively Parallel Simulator; LAMMPS). Fluorine preferentially combines with the network forming cations Si and Al, even when corrected for abundance, but forms longer lived bonds with high field strength elements (HFSEs) Ti and Zr. These species are rarely neutral species, as would be preferred for use in molecular-mixing thermodynamic models, but could be approximated using a neutral oxyfluoride (e.g., AlOF). Alkali and alkaline earth fluorides occur less frequently, but are more likely to form neutral clusters. HF compounds dissociate readily, rarely lasting longer than 100 fs.

Introduction

Rare-metals granite is a class of plutonic rock with abnormally high concentrations of rare metals, including the rare-earth elements (REE; lanthanides, Y, Sc) and high field strength elements (HFSEs) such as Zr, Nb, Hf, and Ta. These metals, especially HFSEs, are not significantly mobile in most fluids, and are geochemically used to trace melting processes, not fluid interactions, which appears to limit the range of possibilities for achieving high concentrations of metals. However, the stability of HFSE and REE compounds in a fluid is significantly improved with the addition of fluorine. This correlation is preserved in the rock record, as many rare-metal granites are also highly enriched in fluorine, particularly granitoids and pegmatites of the NYF (niobium-yttrium-fluorine) variety. However, the final mineralogy of the rocks does not necessarily contain a fluorinated rare-metal phase, like bastnäsite. Instead, it is more common to observe that the magmatic phases include fluorinated phases (e.g., fluorite, fluoroannite) and separate rare-metal phases (e.g., columbite-tantalite). The ores in some of these localities show evidence of post- or late- magmatic alteration and fluid activity, interpreted from the presence of veins, low-temperature phases, and other mineralogical evidence. This poses the questions of what role fluorine plays in the evolution of magmatic systems, its role in the transport of REEs and HFSEs in both fluid and magma, and the stability of its complexes at magmatic conditions. Understanding the behavior of fluorine in these systems would then lead to more informed choices of fluorinated species in thermodynamic models like

MELTS and Perple_X and, in turn, more accurate Gibbs energy models of the melt and fluid phases.

However, geologic processes occur across many conditions and compositions that are challenging to observe or reproduce experimentally. An alternative approach to understanding the phenomenon of fluorinated rare-metal deposits is using computer modelling. Molecular dynamics (MD) can be used to predict the speciation of fluorinated phases over a range of pressure and temperature conditions. However, the most accurate form of MD is *ab initio* (first principle) calculations, which are computationally limited to a small number of particles (typically <100) and short time frames (typically <100 ps; e.g., Boero et al., 2015 and references therein). In order to capture the dynamics of a silicate melt with trace amounts of F and rare metals, simulations would have to be run with at least 1000 atoms and be equilibrated over much longer timescales (>1 ns), especially at the comparatively low temperatures where granitoid magmas exist.. Therefore, empirical force fields, which bypass the quantum mechanical calculations and allow vastly more efficient simulations, would be the more appropriate tool to use. However, such fields have a large number of empirical parameters that must be tuned in order to approximate the behavior of an *ab initio* calculation at a fraction of the cost.

One of the popular potential equations used in MD calculations is the Born-Mayer-Huggins (BMH) equation with a Coulomb term (attractive for cation-anion interactions) and an exponential repulsive term. This equation, described below, has

been applied to fluorinated and halide systems (e.g., Fumi & Tosi 1964a, b; Ida 1976), silicate and oxide systems (e.g., Matsui 1982; Bouhadja et al., 2013), and a limited number of oxyfluoride systems (Wang et al., 2021; Belashchenko et al., 1998). The BMH equation has been parameterized for approximations of geologic systems (Guillot & Sator, 2007a, b), spanning a complex multi-element space (Na-K-Mg-Ca-Ti⁴⁺-Fe²⁺-Fe³⁺-Al-Si-O) over a range of naturally-occurring compositions and conditions. These force fields have enabled simulations that successfully reproduce equations of state and elastic moduli, and allow predictions of atomic behavior that has not been determined experimentally (e.g., viscosity at low temperature).

Methods

ab initio Calculations

In order to evaluate the speciation of F in a complex silicate melt, the interaction parameters for each cation-anion pair were evaluated by fitting forcefields to the depth and shape of energy well determined with *ab initio* calculations. Eight cations (Si, Al, Ca, Na, K, La, Zr, Ti) and two anions (F, O) were evaluated on a pairwise basis, and an additional cation (H) was introduced in ternary compounds.

The *ab initio* calculations were conducted in VASP (Vienna Ab-Initio Simulation Package, Kresse and Hafner, 1993). 19 binary and ternary compounds were sourced from the Materials Project (Jain et al., 2013), as structures that are either predicted or observed to be stable on the convex energy hull. Each compound was equilibrated at

zero pressure using iterative calculations permitting changes to volume and atom positions. These structures were then strained using NVT calculations to vary the volume by $\pm 1, 2, 5$, and 10% change. All volume deviations were hydrostatic in compression or expansion. The settings used in the INCAR files for these are listed in the Supplementary. Systems were run with ISIF = 3 for the volume equilibration, then run with ISIF = 2 for the volume deviations to maintain the strained volume as recommended.

Each of the elements involved were also evaluated at zero pressure to find the per-atom energy included in the energies given by VASP. These calculations were necessary due to differences in the energy definitions used by VASP and LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator; Thompson et al., 2022). Due to complications in the calculations for elemental hydrogen, the per-atom energy for this element was found from the difference between oxygen and water. The energy-volume values were then appropriately converted to the units used in LAMMPS.

Each compound also required a set of calculations to determine the charges of the atoms in the structure, which was accomplished with SeqQuest (Schultz, 2007). For these calculations, the functional used was PBE-SP, the temperature for occupation weighting was 0.003 Ry, the convergence criterion was 0.001 (0.0005 for geometry), and the geometry method was ASD.

Force-Field Calculations

The energy-volume calculations and charges for each compound were then used to calibrate the Born-Mayer-Huggins (BMH) interatomic potential force-fields (e.g., Fumi & Tosi, 1964a, b; Matsui 1982). This formulation of the interaction between atoms is commonly used in MD simulations, as the parameters are transferable between atom types. The BMH potential has many forms (See **Chapter 5**), each of which imposes a set of assumptions. In the original formulation by Tosi & Fumi (1964a), ρ was defined as a constant for all pairwise interactions unique to each ionic crystal (i.e., $\rho_{KF} = x$, $\rho_{NaF} = y$), while Huggins (1953) proposed a constant value for all interactions, regardless of the identity of atoms involved. Sangster & Dixon (1976) treated A_{ij} as a function of the Pauling factors of the ions involved, with or without a per-system constant. Ida (1976) proposed that A_{ij} was equal to ρ times the force constant, an approach adopted by Matsui (1982; 1994; 1996b) and adapted by Bouhadja et al. (2013) to be a unique parameter close in value to Ida. There is also the Buckingham form that combines A and σ into one constant, and this is the form that has been used to fit an approximation of a silicate melt (e.g., Guillot & Sator, 2007a). However, this constant cannot be easily used to determine the cation-cation pairwise interactions and so in this formulation it is necessary to either ignore the BMH terms (Guillot & Sator, 2007a) or fit every set of pairs.

The equation (1) used in this work includes terms pertaining to the Coulombic force, repulsion, and Van der Waals effects between neighboring atoms of types i and j , as

a function of their charge (q), size (σ), separation (r), softness (ρ), and fitting coefficients (A , C , D).

$$U(r) = \frac{q_i q_j e^2}{r} + A_{ij} \exp\left(\frac{\sigma_{ij} - r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} \quad (1)$$

In a binary system with no prior assumptions or constraints, this results in 13 independent parameters. However, several decisions were made to aid in fitting the parameters and to ensure generalizability to the larger simulation. First, σ and ρ were treated as additive (i.e., $\sigma_{\text{Na-F}} = \sigma_{\text{Na}} + \sigma_{\text{F}}$). σ is usually treated this way (Fumi & Tosi, 1964a, b; Sangster & Dixon, 1976). ρ is sometimes treated this way (Ida, 1976), although other authors have fixed it for the entire system (Huggins 1953) or adopted independent values for every pair of atom types (Fumi & Tosi, 1964a). When fitting H-O and H-F interactions, ρ and σ were fit independently of the element-specific parameters in order to better describe the potential (Hauptmann et al., 2003; Cruz et al., 2006). The net charge of the system was assumed to be zero, simplifying two independent charges in a binary structure to one.

Given the complexity of the simulation, the Van der Waals dipole-dipole and dipole-quadrupole forces were ignored. These terms go as $1/r^6$ and $1/r^8$, respectively, and are thus extremely small in a large system. The coefficients on these terms, commonly C_{ij} and D_{ij} , are fixed at 0 for all pairs in this work, an approach many authors take (e.g., Ida, 1976).

As a result of these simplifications, a given binary compound has 8 independent parameters with 9 energy-volume points to be used in the fitting. The settings used in the LAMMPS runs are listed in the supplementary.

The fitting for each compound was conducted independently using the Powell's method solver in Python (Y. Shen, personal communication). The topography of the parameter space for each compound was complex, and free or unbounded searches were unsuccessful, so the initial values were taken from the literature. Previous works that included used the relevant form of the interatomic potential (1) were also used to limit the scope of the parameter space. Several atoms – including Na, K, Si, O, Al, and Ca – have abundant literature that followed similar analytical procedures to the work here (e.g., Bouhadja and Jakse, 2020), which allowed for a well-defined search. Other elements – including H, La, and Zr – lacked such documentation, so systems with these elements were fit after the anion parameters were constrained from other compounds in this work. For parameters with a wide variety of reported constants (most notably for A_{ij}), searches were initialized from each of the reported values, although some of the fitting routines were unable to leave local minima. To assist the fits, the minimum and, occasionally, $\pm 5\%$ volume deviation were more strongly weighted than other data points during general fitting.

Due to a lack of literature data on hydrogen, the energy fits for H_3OF were not successful at reproducing appropriate potentials and bond lengths. As a result, the H-O and H-F parameters were fit manually to match bond lengths from the Materials

Project (Jain et al., 2013). In Table 1, the ρ and σ values for these pairs reflect the total value, not the H contribution.

For cation-cation interactions, the coefficient A_{ij} was determined following the procedure of Janssen & Tissen (1990) by taking the average of the two cations' coefficients (A_{ii} and A_{jj}). The preexponential coefficient for the only anion-anion interaction, A_{OF} , was fit using a ternary compound.

Table 6.1 - Parameters used in the simulation

Atom i	A_{ii} (kcal/mol)	A_{iO} (kcal/mol)	A_{iF} (kcal/mol)	ρ_i (Å)	σ_i (Å)
Na	0.111	0.082	0.729	0.0600	1.2015
Ca	0.069	0.065	0.880	0.0300	1.1830
K	0.236	0.095	0.422	0.0590	1.5285
Si	0.879	0.063	0.939	0.0625	0.7935
Al	0.939	0.063	0.728	0.0765	0.9180
H	0.133	1.283	0.722	0.1385 0.1440* 0.1590**	0.0130 1.323* 1.524**
La	0.566	0.094	1.058	0.0840	1.3235
Zr	0.928	0.051	0.605	0.0335	1.0615
Ti	0.486	0.424	0.851	0.0565	0.9720
O	0.255	-	0.171	0.1445	1.8515
F	0.677	0.171	-	0.1595	1.2520

*H-O parameters indicate the total ρ_{H-O} and σ_{H-O} , fit separately to match bond lengths

**H-F parameters indicate the total ρ_{H-F} and σ_{H-F} , fit separately to match bond lengths

For the main simulation of a silicate melt, the interaction parameters and charges found above were applied. 1242 atoms were placed in a simulation box in a structure based on a feldspar structure, as the distribution of atoms in natural silicate melts is not completely random ([Figure 6.1](#)). The number of each atom type for the variable temperature and pressure runs is shown in Table 2.

Table 6.2 – Elemental abundances in simulation runs

	Number of atoms in named compositions			
Element	Normal	Doped	High F	High H ₂ O
Na	46	40	47	24
Ca	3	14	12	3
K	32	27	41	18
Si	290	258	276	290
La	3	14	3	3
Zr	3	12	3	3
Ti	3	9	3	3
Al	80	87	75	62
H	14	11	14	80
O	763	755	720	751
F	5	15	48	5

Each simulation was initialized with a box relaxation and energy minimization. Following this, it was run with the NVE/limit option, which allows the atoms to un-overlap themselves without the loss of atoms by limiting the maximum distance an atom can travel in a timestep, as is recommended by the LAMMPS documentation (Thompson et al., 2022). Following these initializations, the atoms were run under NPT at a given pressure until the volume stabilized. The bulk of every run followed in a canonical NVT (constant number of atoms, volume, and temperature) ensemble, running for 10^6 fs (1 ns) at the equilibrated temperature with the recommended

damping of 100 timesteps. A list of all run parameters is provided in the Supplementary material.

We also conducted a series of runs with doped starting composition, with elevated concentrations of Ca, La, Zr, and Ti (Table 6.2). In these simulations, additional atoms of these elements were included, adjusting the number of Na, K, Al, Si, and O atoms to maintain a total of 1242 atoms and a net charge of 0. Additional runs with elevated F were run to gain better statistics on these atoms. We also investigated variable H content, as water content in geologic systems is known to strongly affect melt properties, including viscosity and liquidus temperature. All of these altered compositions were run at a fixed temperature of 2000 K to ensure truly liquid-like behavior and to eliminate the effects of temperature on the comparison.

Post Processing

Following runs, the results were primarily analyzed using the Magmatomix/UMD scripts (Caracas et al., 2021). This analysis included calculation of the mean-squared-displacement (MSD), viscosity, and density of states. Analyses of the bonding environments and lifetimes were conducted using a combination of Ovito (Stukowski, 2010) for visualization, UMD scripts (Caracas et al., 2021), and additional python scripts.

Results & Discussion

Force-Field

The validity of the fitted atomic interaction parameters (Table 6.1) was considered for each of the compounds. The initial evaluation was based on the accuracy of the parameters' prediction of the *ab initio* energies. Fits with sum-difference-squared values (R^2) much higher than 1 were considered to be failed, while those with values close to zero were preferred ([Fig. 6.2](#)). For valid fits, common parameters that were independently derived from different compounds should be the same (i.e., σ_{OO} should be the same in Na_2O and CaO). Some slight variations are expected, as the fitting algorithm simultaneously fits 8 parameters, so the average of each parameter was calculated by weighting the values according to the accuracy of the fit. An additional check for attractive atom pairs included plotting the potentials and ensuring that there was a minimum in the potential and at small distances the potential returned to being repulsive.

Values were also considered relative to literature. This was done with caution, as not all authors used or reported the same assumptions in their fitting, and as discussed above, there are different forms of the BMH equation. The most challenging parameter to compare was A_{ij} , as there was very little agreement in the literature, varying up to two orders of magnitude between sources (ex. A_{SiSi} ranges from 0.125-10.166 kcal/mol; e.g., Bouhadja & Jakse, 2013; Delaye & Ghaleb, 1996). For a detailed discussion of the literature, see Chapter V of this thesis.

Simulation

Bond lengths The lengths of cation-anion bonds are presented in [Figure 6.3a and 6.3b](#), for fluorine and oxygen respectively. These lengths are very close to the separations observed in crystals and molecules. As expected, the number of total bonds increases with increasing temperature while the lifetime of bonds decreases ([Figure 6.4](#)). This is due to the higher kinetic energy and atomic velocity breaking up molecules. There is no variation in the average bond length with temperature, but, as the atoms move less at lower temperature, the peaks in the RDFs are sharper in low temperature runs than in high temperature ones.

Speciation In this section, the behavior of fluorine will be described according to the roles of its cation bonding partners in the melt ([Figure 6.5](#)).

The network forming cations are Si and Al. There is no difference in normalized frequency or lifetime of Si-F and Al-F bonds among the four compositions explored, and the expected shortening of lifetimes with increasing temperature is easily observed thanks to the large number of bonds. These are always the most common bonding partner for F, and normalized to the abundance of atoms, are about equal in abundance and lifetime distribution. However, there is almost never sufficient clustering of F about a cation to make a charge neutral species such as AlF_3 or SiF_4 . AlF_3 accounts for $\sim 1\%$ of the Al-F pairs in the high F composition. More commonly, a neutral species can be defined by including a nearby O with the much more abundant AlF^{2+} , forming AlOF . There is no common neutral species involving Si, F, and O.

Na and K are alkali network modifiers, and Ca is the only alkaline modifier in the simulation. In more fluorine-rich melts (“High [F]” and “Doped” compositions), the normalized abundance of bonds Na-F, K-F, and Ca-F bonds all increase compared to the base case, whereas in more hydrous melts (“High H₂O”), the bonds become much less frequent. The alkali-F bond naturally forms a neutral species, but the Ca-F bond is present as a neutral species (CaF₂) in less than 12% of the total pairings. The lifetimes of these bonds are relatively short, with about 60-80% of pairs lasting less than 100 fs and only 4-9% lasting longer than 500 fs. Na-F bonds are generally shorter lived, K-F are longer lived, and Ca-F pairs are usually in between. H is sometimes considered an alkali element, but given its small size, it has special properties. The H-F bond is usually the least frequent pairing, and the bonds are extremely short-lived (97% of bonds last less than 100 fs). This aligns with the known behavior of hydrofluoric acid (HF), which readily dissociates when interacting with silica.

Ti and Zr are representative of high field strength elements in a silicate melt. Due to the small number of atoms, the lifetime population curves are noisier. However, even with the noise, these two atoms have a significant tendency to form bonds with longer lifetimes, with up to 25% of Ti-F and 20% of Zr-F of bonds lasting longer than 500 fs,. The fluorinated species is almost always TiF³⁺ or ZrF³⁺, and never gathers enough F atoms together to be neutral. Zr-F compounds appear to live longer in the “High H₂O” composition, but this is more likely an artefact of the small numbers of Zr-F

bonds that formed over the course of the run in this composition (11 in “High H₂O” compared with 603 in “High F”).

La is a rare-earth element, and in the simulation, La-F bonds have behavior most similar to Ca-F. Bond lifetime distribution is similar to all the alkali/alkaline-F patterns, with about 25% of the bonds lasting longer than 100 fs, and up to 12% of bonds have lifetimes above 500 fs. The most common La-F pairing is LaF²⁺, with less than 1% of pairs involving enough F cluster to form the neutral LaF₃. As with Al, most La-F bonds can be considered part of the neutral species LaOF.

Dynamic Properties Diffusion coefficients and viscosity were calculated from the mean-squared-displacement (MSD) for each element ([Figure 6.6](#)) at all temperatures. Although the MSD plots are linear, which indicates that the simulations achieve the diffusive regime with liquid-like behavior, the viscosities calculated using the Stokes-Einstein-Sutherland equation (Hansen & McDonald, 2006; Allen & Tildesley, 1987) are profoundly non-physical in value (Figure 6.6). Evidently, shear deformation of this melts is not accommodated by self-diffusion of isolated ions, and viscosity must be calculated in a different way.

Limitations of the Simulation

While a simulation may be an energetically accurate description of the physical chemistry of atoms, it is not guaranteed that it is a reflection of the natural system. The primary limitation of modelling magmatic systems is that they are naturally complex, including complicated chemical make-ups (i.e., major, minor, and trace

elements), temporal variability, and open system boundaries. Magmatic flow and the transport of fluids change the composition and conditions (i.e., pressure, fO_2) of the magma. Magmas are also understood to be a mixture of melts, crystals, and fluids (vapors), including both phases generated from the magma itself and those inherited from the surroundings.

There is also difficulty in comparing the results of natural, laboratory, and simulated systems due to the differences in the time scales. For example, the time examined when measuring diffusion ranges from years and millennia to minutes and hours to femtoseconds and nanoseconds, respectively (de Koker & Stixrude, 2010). In this work, one of the main limitations is the absence of iron, a major element in magmatic systems. Fe was omitted due to the complications pertaining to the oxidation state (i.e., Fe^{2+} or Fe^{3+}), which would need to be explicitly imposed on the system (Guillot & Sator, 2007a), asserting the oxygen fugacity of the magma. Fe, and to a lesser extent Ti, would require additional terms in the interatomic potential, namely the Morse potential (e.g., Xu et al., 2013; Rittirum et al., 2016), which helps to describe the interaction of metals and metal oxides. Previous studies that used the BMH potential alone to describe Fe (Guillot & Sator 2007a) report unusual behavior of the potential at high concentrations of Fe or poor reproduction of experimental results (Lewis 1985). The differences may be due to the unincluded metal-metal interactions or the presence of occupied d orbitals. Given that previous studies do not

report the same issue with Ti (Jakse et al., 2021), the lack of *d* orbital electrons in Ti^{4+} may obviate the need for a Morse term.

Additionally, this simulation only investigates the high silica composition, even though lower silica (<60% wt.% SiO_2) granitoids exist. As indicated in Chapter 3 of this thesis, a wider range of peralkaline and peraluminous compositions should be explored to see if the different F-HFSE behaviors occur on an atomic level.

Conclusion

Modeling methods are used to investigate the behavior of complex natural environments, including magmatic systems. However, informed models require descriptions of atomic interactions, which can be determined with molecular dynamics. This work presents the definition of the Born-Mayer-Huggins approximation of an eleven component system (F-Na-K-Ca-H-Si-Al-Ti-Zr-La-O) to interrogate the speciation of fluorine within a silica-rich magma. Most common F bonds are present with Si and Al, although the species formed are generally not neutral. However, Al-F bonds may be made neutral with the inclusion of a neighboring O (AlOF). Alkali and alkaline earth element pairs with fluorine are common, neutral, and short lived while high field-strength rare-earth element pairs are infrequent, charged, and long lived. Therefore, the most representative and thermodynamically feasible species with which to introduce F is AlOF.

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Figures

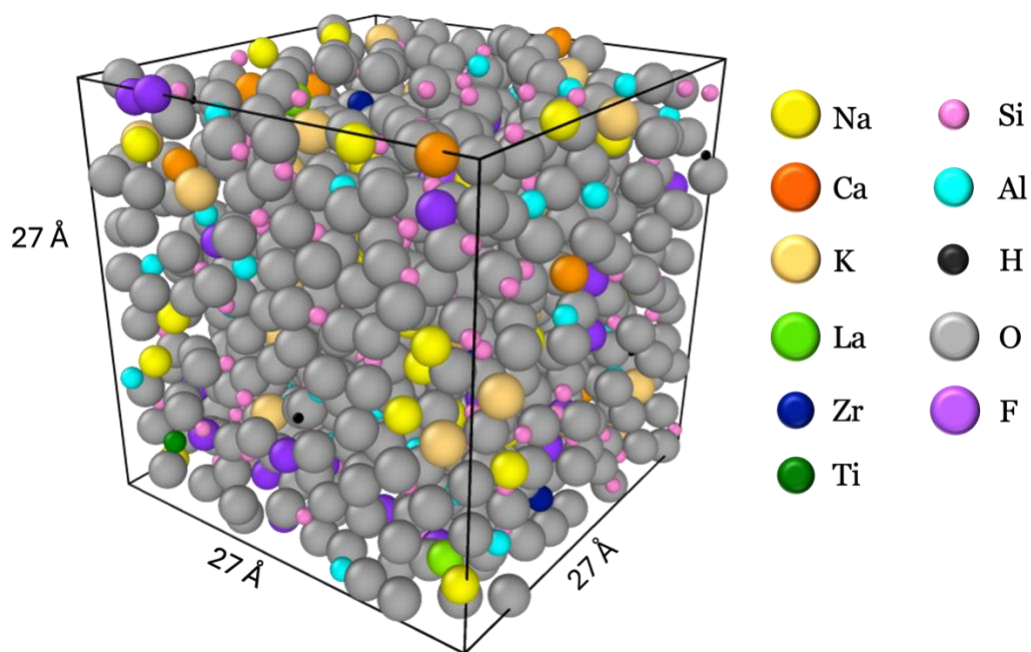
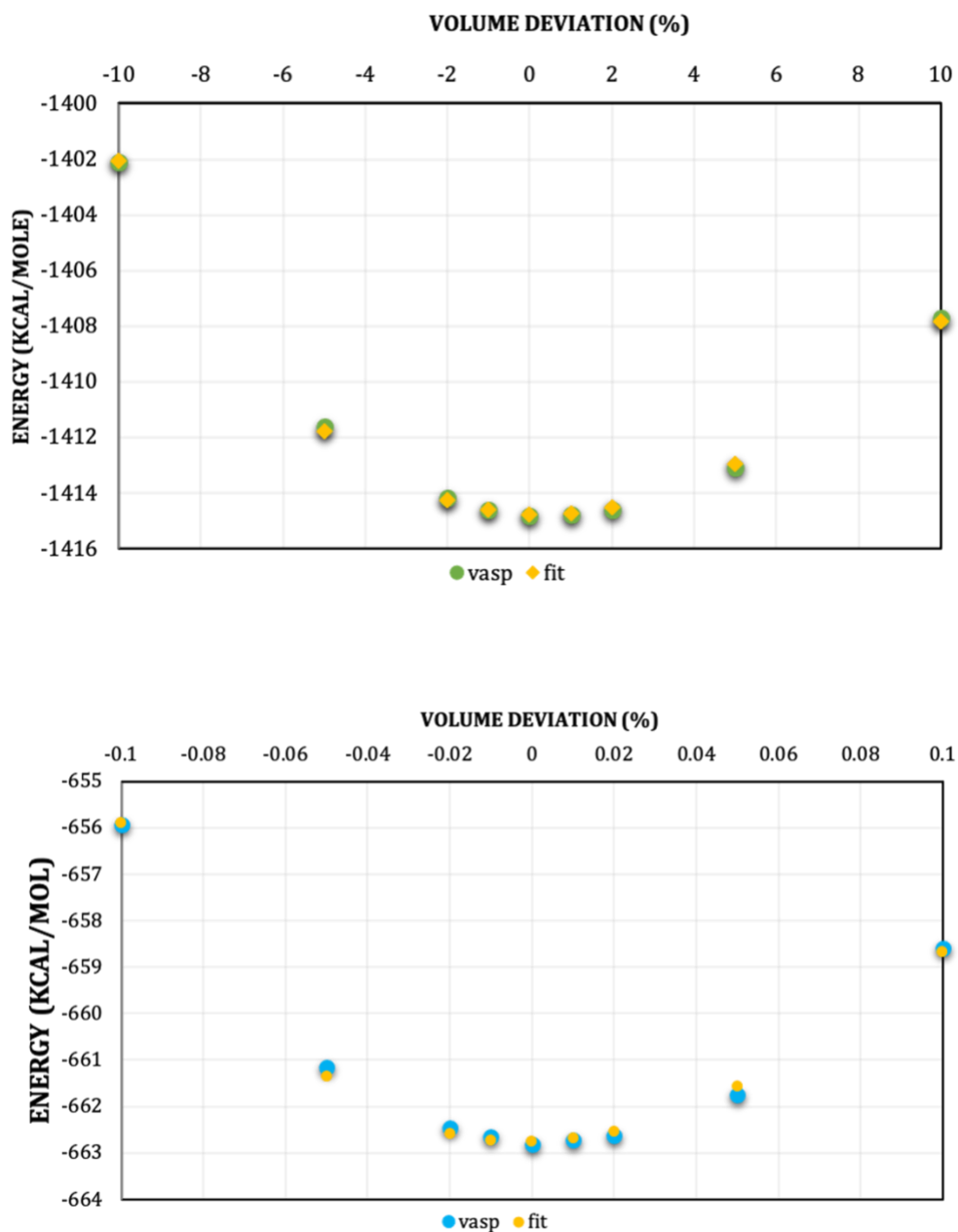


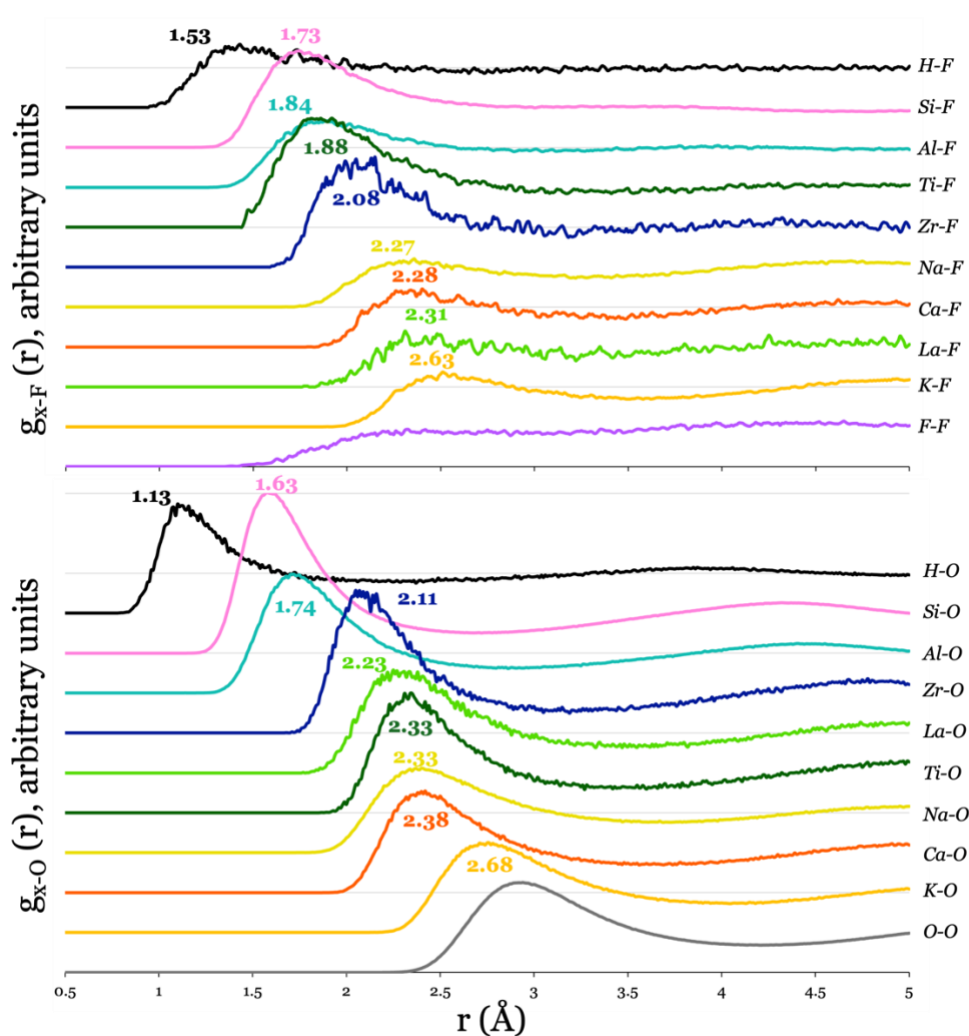
Figure 6.1 – Example of simulation cell.

Still taken from the “High [F]” composition. The atoms investigated are presented in the legend and are initially placed in a feldspar-like structure, although after initialization, the cell is no longer ordered. The sizes are not true ionic radii, but are slightly scaled. Image generated with OVITO (Stukowski 2010).



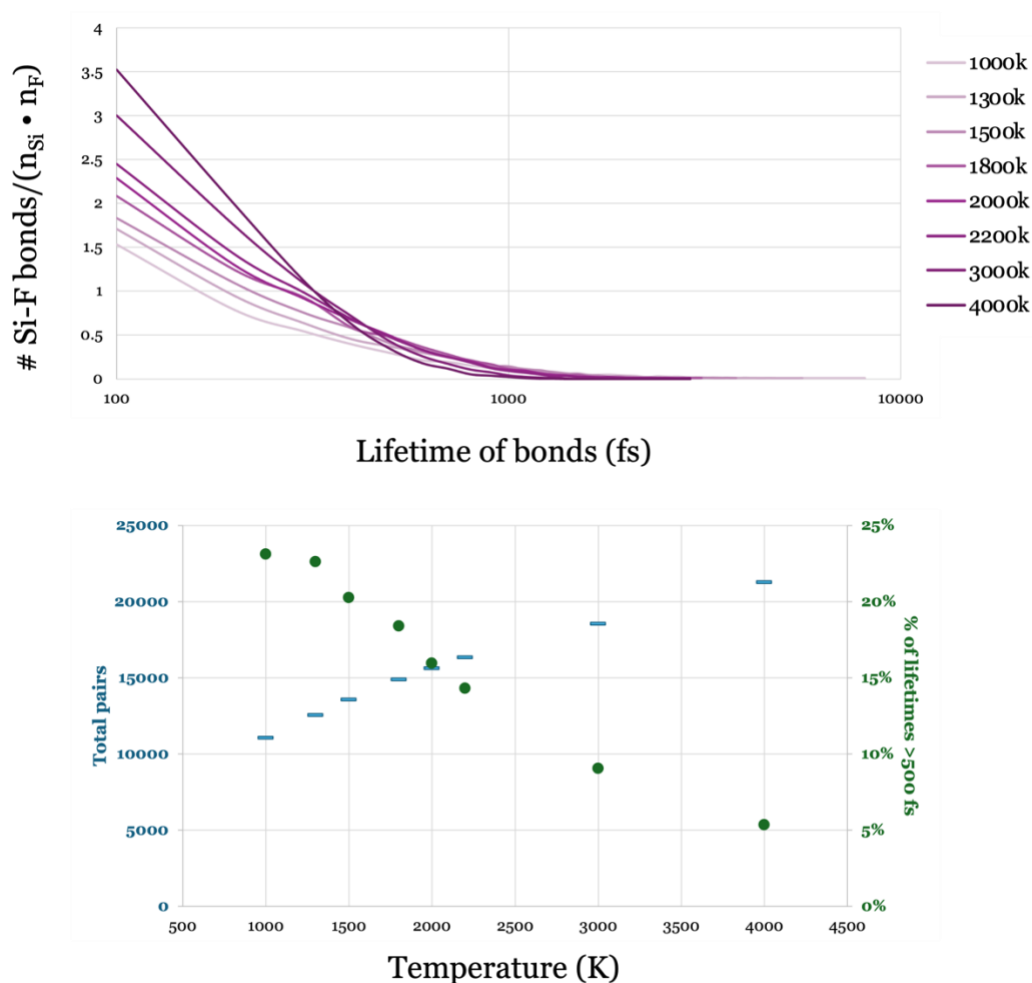
[Figure 6.2](#) – Ab initio and force-field fitting.

Examples of the ab initio energy well about the crystal equilibrium volume and the best-fit force field for CaF₂ (top) and K₂O (bottom). In both, the difference between the ab initio and force field calculations are extremely small.



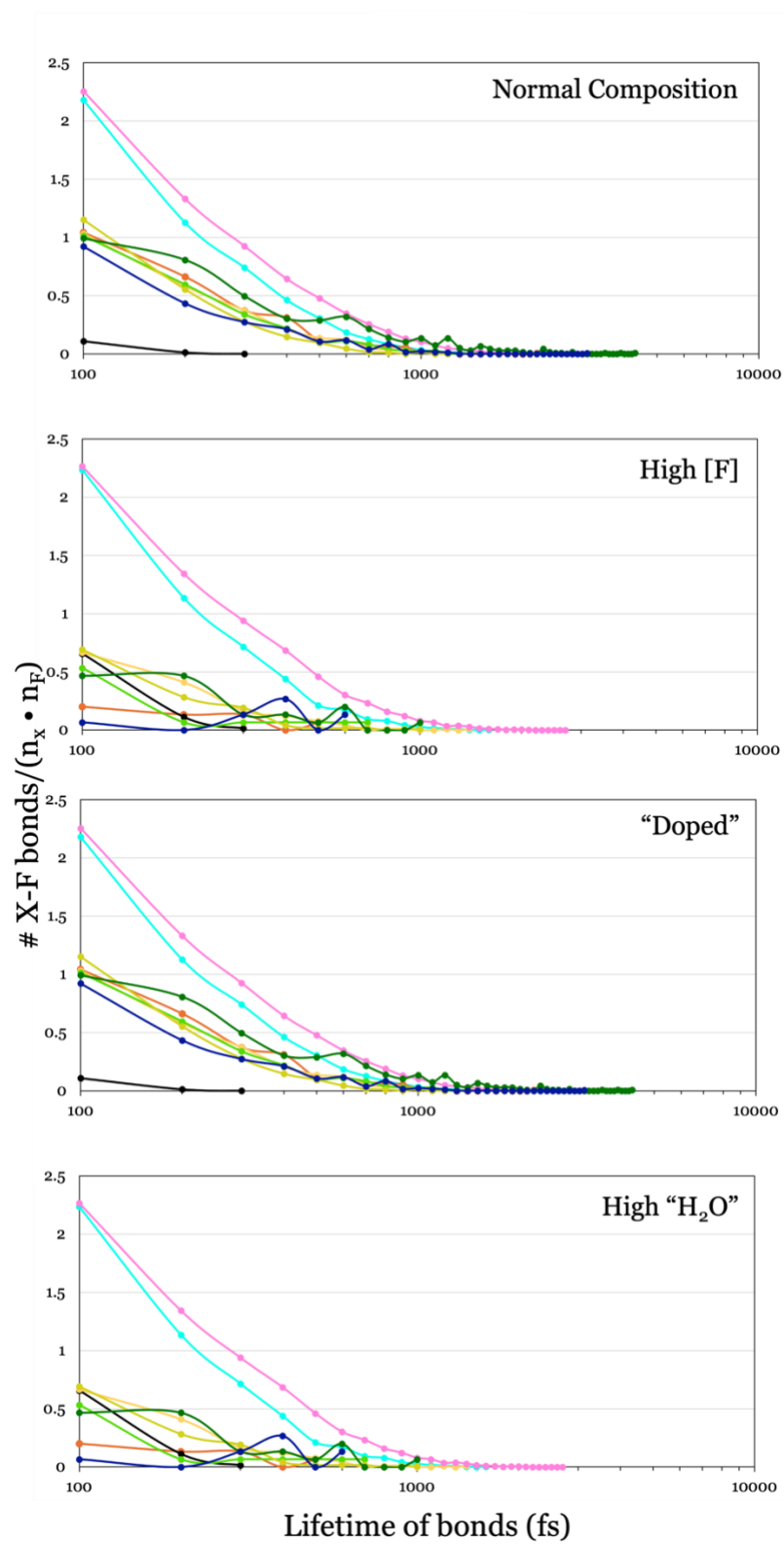
[Figure 6.3](#) – RDFs for cation-anion pairs

Partial radial distribution functions (RDFs) for cations with F (top) and O (bottom) in the “High [F]” composition. The RDFs have been normalized to converge to 1 at large distances, and are offset for clarity. The first maximum, or the typical bond length, has been labelled for bonding pairs. The smoothness of the functions is dependent on the number of atoms involved, so trace elements have noisier patterns than major elements.



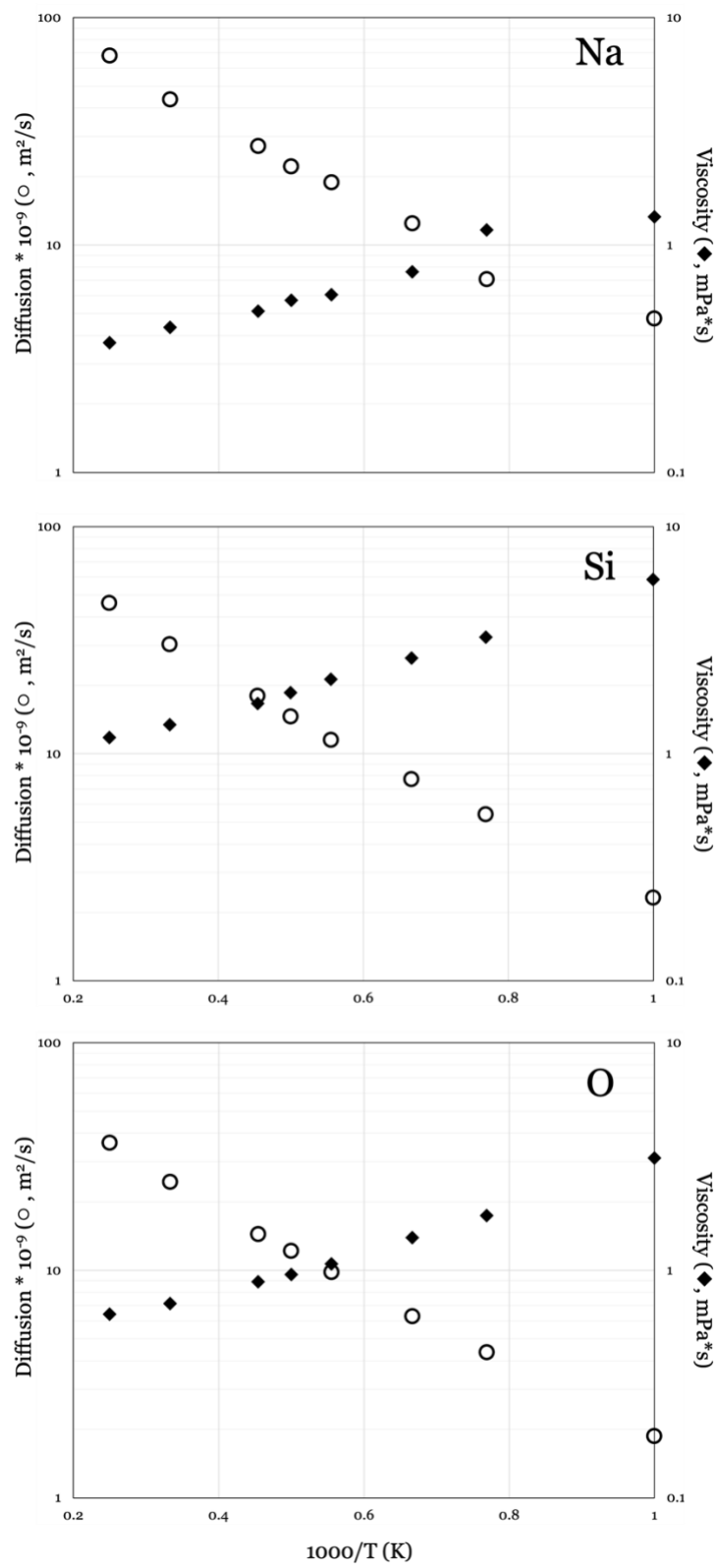
[Figure 6.4](#) – Bond behavior as a function of temperature.

(top) The distribution of Si-F bond lifetimes for each temperature, the number of bonds for a given element pair increases (normalized to atom abundance), while the lifetimes of these bonds trend toward smaller values. (bottom) A plot of the total number of pairs (left axis) and the percentage of “long-lived” pairings (>500 fs; right axis) as a function of temperature.



[Figure 6.5](#) - Bond behavior as a function of composition at 2000K.

These histograms show the distribution of bond lifetimes for a given cation-F pair (normalized to atom abundance) is shown for simulations with (from top to bottom) normal composition, a “doped” composition, a high [F] composition, and a high “H₂O” composition (high [H]). The colors of element pairs as in Fig. 6.1 and 6.2. Network elements like Al and Si show no strong dependence on trace element composition, while alkali network modifiers like Na and K create more pairings with F in high [F] simulations and fewer pairings in “high H₂O” simulations



[Figure 6.6](#) – Calculated diffusion and viscosity.

Diffusion and viscosity profiles for (from top to bottom) Na, Si, and O across the range of temperature simulations. Diffusion (circles, left axis) is calculated from elemental MSD and viscosity (diamonds, right axis) is calculated using the Stokes-Einstein-Sutherland equation assuming viscous flow is controlled by diffusion of the atom in question, demonstrating the non-physical values.

Appendix

Supplementary Files in Deposit:

- Run conditions for VASP and LAMMPS
- Log Files for all Force-Field data collection runs
- RDF and MSD Files, as generated by UMD/Magmatomix
- .xyz files available upon request (each is ~2GB)