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The role of fluorine in the concentration and transport of lithophile trace elements in felsic magmas: Insights from the Gawler Range Volcanics, South Australia

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A B S T R A C T

Rhyolites of the Mesoproterozoic Gawler Range Volcanics (GRV) of South Australia are characterised by high concentrations of some trace elements (REE, Y, HFSE, Rb and F, in particular). Whole rock geochemical data suggest that these elements were incompatible during magma crystallisation. Accessory minerals (fluorite, zircon, REE-F-carbonate, Ti oxide, apatite, and titanite) can account for most of the trace element content of the rocks. These minerals occur in vesicles, micromiaroles, lithophysal vugs and in interstices between major mineral phases (quartz and feldspar as both phenocrysts and groundmass). Such textural evidence indicates that accessory minerals crystallised late in the history of the magma and that they were deposited from a volatile-rich (fluid) phase. These features are explained by the following sequence of events: 1) F dissolved in the magma lowered the crystallisation temperature of accessory minerals, causing trace elements (REE, Y, and HFSE) to behave as incompatible elements. 2) Protracted crystallisation of major mineral phases (quartz, feldspar, and oxides) formed a volatile- and trace element-enriched residual liquid. 3) A volatile element (H_2O, F, and CO_2)-rich phase (late-stage magmatic fluid) evolved from the magma. High concentration of fluorine and other complexing agents in this phase allowed trace elements to be transported in solution. 4) Accessory minerals crystallised from such a phase in vesicles, micromiaroles and interstices between the major mineral phases.

1. Introduction

Fluorine (F) plays an important role in several processes occurring in magmas and associated fluids. Experimental studies indicate that F dissolved in silicate liquids strongly influences phase equilibria by decreasing solidus temperature and shifting the eutectic composition away from quartz in the granitic ternary diagram (Manning, 1981). Fluorine reduces viscosity and increases ion diffusivity in silicate melts (Dingwell et al., 1985; Giordano et al., 2004). Fluorine has also been shown to have a major influence on the activity coefficients of trace elements in magmas by increasing the solubility of zirconium and other high field strength elements (HFSE) (Keppler, 1993). The capacity of halogens (F and Cl) to bond with and to transport lithophile elements (e.g. REE, Nb, Th, U, Ba), commonly considered as immobile in an aqueous fluid (e.g. Cullers et al., 1973; Lesher et al., 1986; Michard and Albarède, 1986; Möller et al., 2003), has been confirmed by experimental data (London et al., 1988; Webster et al., 1989; Keppler and Wyllie, 1990; 1991). Evidence indicating the association of these elements and F-bearing mineralising fluids has been reported by several authors in different natural systems, including felsic magmatic systems (Gieré, 1986; Charoy and Raimbault, 1994; Audétat et al., 2000; Webster et al., 2004; Schönenberger et al., 2008), metamorphic rocks (Gieré and Williams, 1992; Pan and Fleet, 1996; Rubatto and Hermann, 2003). This paper reports the presence of late-formed aggregates of F-, REE (lanthanides, U, and Th)-, Y- and HFSE (Ti, Zr, and Nb)-rich minerals filling vesicles, micromiarolitic cavities and lithophysal vugs in rhyolitic units of the Gawler Range Volcanics of South Australia. These minerals indicate mobility of such elements in the late magmatic stage. We also discuss (1) the characteristics of the phase (here referred to as late-stage magmatic fluid) that transported these elements, as inferred from mineralogical and textural data, (2) the role of complexing agents in the transport of REE and HFSE and (3) the capacity for F-rich magmas to produce distinctive trace element-rich late-stage magmatic fluids.

2. Vesicles, micromiarolitic cavities and lithophysal vugs

Despite textural differences, vesicles, micromiarolitic cavities and lithophysal vugs share a common origin as a consequence of magmatic volatile element concentration and imply the presence of a volatile-rich, alumino-silicate-poor fluid phase (Roedder, 1981; London, 1986). This phase can be permanently entrapped on solidification and crystallise in situ, and evidence of its characteristics can be preserved by minerals precipitating in these cavities.

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Vesicles form in lavas, shallow intrusions and densely welded pyroclastic facies as a result of exsolution of a volatile phase (McPhie et al., 1993). Miarolitic cavities (miaroles) can be found in shallow intrusions and comprise crystals of magmatic, super-solidus minerals projecting into either a cavity or a mass of hydrothermal minerals (London, 1986; Candela, 1997; Kile and Eberl, 1999). Such "external" nucleation of super-solidus minerals (nucleation on the former fluid phase interface) determines the irregular shape of these cavities (Candela and Blevin, 1995; Candela, 1997). Lithophysae consist of radially oriented crystallites, sometimes concentrically chambered, distributed around a circular to star shaped vug (McArthur et al., 1998). They occur in lavas and welded pyroclastic deposits and can reach a few tens of centimetres in diameter. The central vug forms during crystallisation and it may remain open or be lined or filled with minerals (McPhie et al., 1993). Although the origin is debated, ductile or ductile–brittle deformation of lithophysae provides evidence for high-temperature crystallisation within the melt (Cas and Wright, 1987; McArthur et al., 1998 and ref. therein).

3. Geological setting and sample description

3.1. Geological setting

The Gawler Range Volcanics (GRV) and co-magmatic Hiltaba Suite (HS) Granite represent a silicic large igneous province with an outcrop extent of more than 25 000 km^2 and a total estimated magma volume of 100 000 km^3 (Blissett et al., 1993; Fig. 1). The volcano-plutonic province was emplaced in an intracontinental setting in the Mesoproterozoic, during the Laurentian supercontinent assembly (Blissett et al., 1993; Allen and McPhie, 2002; Allen et al., 2008). U–Pb zircon dating of the GRV has yielded ages of 1591–1592 Ma (Fanning et al., 1988). The HS granite has ages that span a time interval between 1583 ± 7 and 1598 ± 2 Ma (U–Pb zircon dates; Flint, 1993). The giant Cu–Au–U ± Ag Olympic Dam deposit is hosted in the GRV-HS province. The deposit is enriched in REE and F compared to crustal values (Bailey, 1977; Hu and Gao, 2008). The units in the GRV range in composition from basalt to rhyolite and mainly comprise lavas and

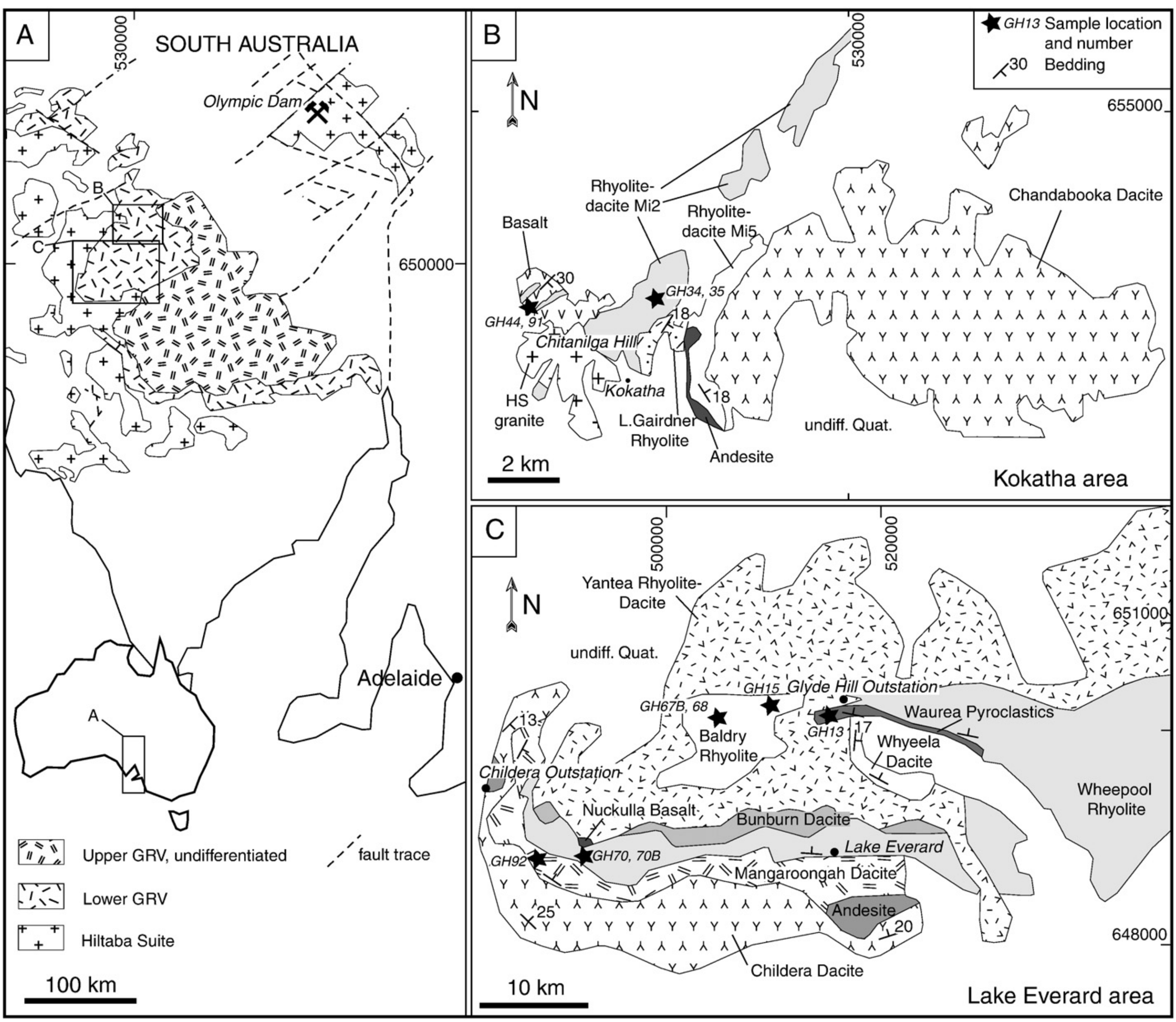

Fig. 1. Simplified geological map of the Gawler Range Volcanics and Hiltaba Suite granite (A), Chitanilga Volcanic Complex at Kokatha (B) and Glyde Hill Volcanic Complex at Lake Everard (C). After Blissett (1975, 1993). Grid: GDA94.