# PROGRESSIVE ALBITISATION IN THE "MIGMATITE CREEK" REGION, WEEKEROO INLIER, CURNAMONA

Thesis submitted for the degree of Master of Science Geology &Geophysics School of Earth & Environmental Sciences The University of Adelaide

by

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## **1 INTRODUCTION**

The study area follows a creek (called here Migmatite Creek) and is located on the Walparuta Inlier of the Curnamona Craton, approximately 356 km northeast of Adelaide and 25 km north of Manna Hill. The nearest private homestead is Weekeroo Station, located c. 6 km south of the study area (Figure 1.1). The mapped area is about  $3 \text{ km}^2$  (2 km × 1.5 km), and situated between latitudes 32° 13' and 32°14' south and longitudes 140°02' and 140°04' east (from E 0408600 to 0410800 m; N 6334000 to 6435400 m in GPS data of map in GDA 94).

The area is part of the inliers of basement, west of the Olary Domain. The stratigraphy is dominated by the Curnamona Group of the Palaeoproterozoic Willyama Supergroup. All lithologies are metamorphosed to amphibolite grade with partial melting or migmatisation common throughout the sequence. Known mineralisation in the area consists of subeconomic Au - Cu - Zn -U as found elsewhere in the Olary Block. Outcrops of Au - Cu - Zn mineralisations surround the area. The nearest mine is the Walparuta Cu-Au Mine, south of the area. The most prominent types of alteration are a pervasive albitisation and associated biotite alteration.

#### 1.1 Background

Pervasive and intensive albitisation variably affected almost all rock types in the study area. Kent et al. (2000) indicated that albitisation affected most rock types and linked this to other types of alterations in the Olary Domain of the Curnamona Province. Three styles of albitisation were distinguished as i) Na-Fe alteration, ii) Na-Ca alteration and iii) late stage albitisation (Ashley et al. 1997; Conor 2006; 2004). Ashley et al. (1998) and Clark et al. (2005) suggested that both albitisation and calcsilicate alteration were related to fluid flow or fluid/rock interaction during Mesoproterozoic shear zone activation in the Olary Domain.

This project characterises albitisation of lithological units for determination of both mobility of elements and influence on REE and trace elements. Albitisation gradient mapping has not been previously attempted. REE patterns may provide insight into the sources and evolution of both fluids and rocks. However, REE changes due to albitisation have not been previously investigated systematically for the regional scale albitisation found in the Weekeroo Inliers and thus the influence of albitisation on REE has not been previously identified. New geochemical methods and techniques can provide further in depth information about albitisation and identify the potential of mineralisation and thus support exploration.

## NOTE:

This figure is included on page 2 of the print copy of the thesis held in the University of Adelaide Library.

Figure 1.1 Geological overview and location of the Migmatite Creek Region (after Laing 1995).

The changes in composition of fluids can be estimated by using whole-rock composition data. Calculation of isocons provides detailed insight into the process of enrichment/depletion of elements during albitisation. The chemical equilibria of fluid/rock can be linked to changes of REE patterns of rock and mineral re-assemblages in stages of alteration. The REE patterns also provide information about the origin and

evolution of rock types and source(s) of fluids and metals. The details of the changes can be associated with mineralisation, e.g. Iron-Oxide-Cu-Au-U-REE deposits in the area.

This project aims to improve the knowledge about lithological variations and element exchanges, and to support mineral exploration in Curnamona and elsewhere.

#### 1.2 What is albitisation and why is it important?

Albitisation can be defined as a process of sodic alteration in which the affected rock is partly or completely replaced by albite. This process has been recognized in a wide range of geological settings throughout the earth's history. It occurs from early diagenesis to well into the amphibolite facies, and may affect all rock types (Williams et al.1999). Oliver et al. (2004) pointed out that albitisation should be seen as a metal mobilising process which indicates its relevance for processes leading to the formation of mineral deposits. In the area of the Telechie shear zone, Olary Domain, Clark et al. (2005) suggested albitisation was the first stage of fluid flow which was involved in the addition of Na and loss of Si, K and Fe. Thus by definition albitisation should be seen as an altering process, related to fluids interacting with rocks and producing mainly albite.

Understanding albitisation is essential to understand the related complex alteration and mineralisation systems. As a secondary process, albitisation may produce K-Fe and Ca-Si alteration linked to the selective mobilisation of K, Fe, Mg and Ca (Oliver et al. 2004; Clark et al. 2005). Albitisation and related alteration assemblages are spatially associated with most IOCG systems, e.g. Iron Skarn-type, Bayan Obo-type, Kiruna-type, and Phalaborwa-type (Corriveau 2006) and have been suggested for the Broken Hill Ag-Pb-Zn deposit (Corriveau 2006; Skirrow 2003; Bierlein et al. 1996). Albitisation and associated hydraulic breccias are found in most IOCG provinces and are pervasive and intense in the Olary Domain (Conor 2004). Albitisation overprinted metamorphic migmatites and possibly affected all lithologies in and adjacent to the Migmatite Creek area (Laing 1995; Conor 2004). The resulting albite replaced most minerals, producing "spent" metal-rich fluids, and in the area of study may be linked to possible Cu-Au mineralisation.

#### 1.3 Basics of Mineral Chemistry and Mineralogy

Albite is an end member in the feldspar series of albite  $(NaAlSi_3O_8)$  + anorthite  $(CaAl_2Si_2O_8)$  + orthoclase  $(KAlSi_3O_8)$  (Figure 1.2). The nominal composition of albite is normally about 8.30 wt% Na, 0.76 wt% Ca, 10.77 wt% Al, 31.50 wt% Si and 48.66 wt% O (<u>http://webmineral.com/data/Albite.shtml.3/06/2006</u>). Albite can be formed during metamorphism and metasomatism, and in pegmatites and magmatism through fluid circulation and related to mineralising systems.

Plagioclase is the series of albite (Ab) + anorthite (An) at variable ratios of Na/Ca. Plagioclase contains less than 10% of Or plus An. The series of plagioclase is divided into albite (0-10% An), oligoclase (10-30% An), and esine (30-50% An), labradorite (50-70% An), bytownite (70-90% An) and anorthite (Shao 1978).

Alkaline feldspar is the series of albite + orthoclase and consists of minerals at variable ratios of Na/K stable at elevated temperature. The series of Ab-Or also may contain <10% of Anorthite. Recent research has redefined the range of temperature for forming albite, expanding it to the range from 300°C to 600°C (Williams & Skirrow 2002; Tan et al. 2004; Teale et al. 2002; Robert et al. 2002; Requia & Fontbote 2002; Smith & Wu 2002).

NOTE:

This figure is included on page 4 of the print copy of the thesis held in the University of Adelaide Library.

Figure 1.2 The mixing series of Or-Ab-An at variable temperature (From Shao 1978).

#### 1.4 Albitisation: a global overview

Albitisation was recognized globally as an important aspect of alteration, mineralisation, metamorphism, metasomatism and crustal brine systems. Various sources have been suggested for the Na-rich brines causing albitisation: i) leaching of halite from exhalatives (Bierlein et al 1996), ii) the dissolution of evaporites (Bierlein et al. 1996) and iii) dehydration reactions (Clark et al 2005; McCaig et al. 1990), iv) magmatic fluids, v) fluids derived through devolatilisation of sodic volcanic rocks, vi) seawater interaction, vii) intraformational Na-rich brines. Albitisation is thought to form predominantly at variable high temperatures and high pressures, although it also forms at low temperature and pressure of supersaturated fluids (Williams & Skirrow 2002; Requia & Fontbote 2002; Smith & Wu 2002). Conventionally it is believed that the fluids are of neutral pH to alkaline and mostly oxidised (Strauss 2003; Niiranen 2005; Mark et al. 2006).

#### 1.4.1 Geological Settings

Albitisation is found globally and throughout the earth's history (Table 1). It may affect all types of rocks: igneous, metamorphic and sedimentary, e.g. basalts at Kibambale in central Shaba, Zaire; the Proterozoic slates and schists, Bayan Obo, China and Permian – Triassic sediments, Western Cornwall, UK (Table 1). The geological settings of albitisation predominate in continental arc and intracratonic settings, mostly in the Proterozoic (Table 1).

Albitisation fluids normally flowed preferably in pathways defined by regional tectonic/structural margins, crustal scale faults, shear zones and other high permeability zones. Albitisation may be accompanied by the different scale geological/geothermal events such as basin extension, basin reversion, fluid circulation and orogeny.

The tectonic settings of prominent albitised sequences bear a similarity to those of Iron Oxide – Copper – Gold (IOCG) systems (Mark et al. 2006; Corriveau 2006; Hunt et al. 2005; Allibone 2004; Bassot 1997; Vandehaar 1993; Teale & Fanning 2000). Examples include the Wernecke Mountains, Yukon, Canada (Hunt et al. 2005) and iron-oxide Cu - Au (- Zn - Ag) mineralisation, Chilean coastal Batholith (Robert et al. 2002) as well as a diversity of epigenetic Cu-Au mineralisations, Cloncurry district, Australia (Mark et al. 2006) (Tables 1 and 2). Albitisation is related to the specific sub-types of IOCG mineralisations in five districts: i) the Cloncurry district, Australia e.g. Ernest Henry IOCG system (Williams & Skirrow 2002); ii) the Punta del Cobre Salobo, Brazil, South America (iron oxide-Cu-U-Au-REE deposits) (Requia & Fontbote 2002); iii) North Sweden (Cu-Zn-Pb-Ag-Co Au mineralization) (Carlon 2002); iv)Bayan Obo, China (Fe-REE-Nb deposit) (Smith & Wu 2002); and v) Palabora, South Africa (the end-member of IOCG systems) (Barton & Johnson 2004; Corriveau 2006; Groves & Vielreicher 2001).

According to Conor (2004), albitisation events in the Curnamona Craton were widespread, intense, pervasive mainly hydrothermal processes concurrent with phases of structural/tectonic evolution. Kalkaroo and Portia are the localities for examples of possibly diagenetically-formed albitite. Three types of albitisation were identified during the Olarian Orogeny:

1) Na-Fe alteration marked by the formation of albite and magnetite (in psammites, pelites, psammopelites, schists, composite gneiss, amphibolite, volcanics, granofels and laminated quartzofeldspathic rocks, etc) e.g. in the George Mine Formation in the Dead

Horse area, Basso Suite. The Na-Fe alteration was suggested to be the diagenetic stage, dominant in the psammite units.

2) Na-Ca-Si alteration combines the assemblage of albite, actinolite, diopside and quartz as well as intensive brecciation for example in the Cathedral Rock area. The Na-Ca-Si alteration mostly affected the Ca-bearing lithologies with indications of a structural control.

3) Late stage albitisation consists of cherty albite, quartz albite near the deposits (Pb-Zn) in the Benagerie Ridge area and it is also widespread (Conor et al. 2004). The late Na-Si alteration is linked to breccias, the fold hinges,  $OD_3$  and overprinting on pegmatite and migmatite. This late stage albitisation was active at high temperature (400-475°C) and high pressure (300-600MPa) during activity of shear zones and synchronous fluids flow in Telechie Valley (Ashley et al. 1997; Clark et al. 2005).

Numerous examples of Na or Na – Ca alteration cut by the granites (Ninnerie Supersuite, U-Pb dating 1596-1575Ma) is probably around during the closing stage of the Olarian Orogeny and during the granite generation. Clark et al. (2005) indicated that albitisation and calcsilicate alteration in the Curnamona Province was synchronous with shear zone activation at mid-crustal levels in the Willyama Supergroup at  $1582 \pm 22$  Ma, between the end of the Olarian Deformation OD<sub>3</sub> and the regional emplacement of S-type granites.

Albitisation in the study area at the Migmatite Creek was suggested to be the late stage type controlled by up to km-scale antiformal folding (Ashley et al. 1997; Conor 2004; Clark et al. 2005). Pegmatites are common in the area and possibly related to the migmatization. The relationship between albitisation and the migmatization is not completely clear.

#### 1.4.2 Albitisation and Mineralisation

Sixty percent of IOCG deposits, which are Iron Skarn-type, Kiruna-type, Phalaborwatype and Bayan Obo-type, are associated with a form of albitisation that surrounds the deposits, and is thought to have produced the metal rich ore fluids and related alterations. Skirrow (2003) and Bierlein et al. (1996) documented that at least three stages of albitisation at 1-2 km depth were responsible for the Broken Hill type mineralisation, linked to metamorphism and granite intrusive events. Additionally, albitisation is spatially linked to some well-studied IOCG deposits e.g. in Canada, Finland, Norway and Peru. Albitisation can be associated with a wider range of mineral deposits, such as the Broken Hill types of Ag-Pb-Zn systems (Stevens 2003; 2006); base metal W, Sn, Mn, Sb, Bi, Mo, Ni, Co, Ba deposits as well as the non-metal As, F and P deposits. Albitisation also occurred in the Bronzewing lode-gold deposit, Western Australia (Eilu et al. 2001) and the semi-massive iron sulphides and gold mineralisation, Disko Bugt, central West Greenland (Stendal 1998; Kalsbeek 1992), Albitisation related to different types/styles of mineralisation can be very variable depending on geological settings, like extensional basins or large scale breccia systems, tectonic or structural setting and lithological combinations. For example, initial albitisation was responsible for the formation of secondary K-rich fluids followed by the co-evolution K-rich fluid leading to K alteration surrounding the magnetite deposits e.g. in northern Finland (Niiranen 2005; Eilu et al. 2001), and Disko Bugt, West Greenland (Kalsbeek 1992). The intensity of Sn-Nb-Ta mineralisation was directly dependent on the intensity and extent of imposed albitisation (Lamba et al. 1988). In the Eastern Fold-Belt of the Mt Isa Inlier, albitisation is associated with most of the Cu-Au deposits and coincided with the emplacement of the Williams/Naraku batholiths and the regional brecciation and Na-Ca alteration. The Osborne deposit was a significant exception; a long period- multistage albitisation possible provided the ground or preparing metals for varies stage of mineralisation (Rubenach & Sayab 2004). Here extensive albitisation, biotite alteration and localized Na-Ca alteration predate the metamorphic peak, and were not obviously related to igneous intrusions (Mark et al. 2004).

Further mineralising processes potentially related to regional albitisation are through separation of the alkali elements Li and Be from albitisation fluids due to changes of pH. Gem tourmaline and beryl mineralisation can result as for example in Be- and Li-Be type pegmatites in Brazil (Preinfalk et al. 2000). The F  $\pm$  (Li, REE, Y, Nb, Ta, and Sn) contents were enhanced during albitisation to produce F-rich mica associated with disseminated-type topaz-columbite-cassiterite mineralisation (Sakoma et al. 2000).

In Ordovician to Triassic units at Hebei, China, complex albitisation mineral assemblages were spatially connected to Fe-REE-Nb deposits (the world's largest REE resource) (Smith & Wu 2002). Finally, Chabiron et al. (2003) indicated that albitisation was the first stage of silicate alteration sequences in the extensive uranium mineralisation systems in the Streltsovka caldera (Transbaikalia, Russia). To summarize, albitisation was associated with at least four styles of mineral deposits and displayed general similarities of geological setting and Na-rich fluids but with obvious variability in detail.

Albitisation in the Olary Domain of the Curnamona Province affected all rock types to variable degrees as a regional phenomenon, and is frequently spatially associated with calcilicate alteration and breccias. Rocks affected by albitisation as well as calcilicate alteration/brecciation contain magnetite, hematite and sometimes pyrite and chalcopyrite mineralisation (Conor 2004). However, the genetic relationships of albitisation to mineralisation are not clear yet. Some diagenetic albitisation may have formed at the same time as basin extension about 1720 Ma for the earliest Curnamona Group (Conor 2004). The other two main albitisation events can be related to the Olary Orogeny (1600-1580 Ma) and a possible mineralizing event (1610-1630Ma) relating to widespread Na-Fe-Ca metasomatism (Skirrow 2003; Conor 2004).

| Area            | Time  |   |   |   |   |  |  |
|-----------------|---|---|---|---|---|--|--|
|                 | Archaean  | Proterozoic   |   |   | Palaeozoic  | Mesozoic,<br>Cainozoic   |  |
|                 |   | Palaeo-   | Meso-   | Neo-  |   |  |  |
| Australia       | Yandal<br>greenstone belt,<br>Western Australia<br>1  | Eastern Fold Belt,<br>Mt Isa Inlier <sup>2</sup><br>Broken Hill                         | Olary<br>Domain <sup>3</sup><br>Eastern<br>Gawler<br>Craton <sup>22</sup> |   | NW Tasmania⁴  |  |  |
| America         | Carajas, Northern<br>Brazil <sup>7</sup>  | Wernecke<br>Mountains, Yukon,<br>Canada <sup>5</sup>                                    |   |   | (S-O, 445–425 Ma)<br>Northern New<br>Brunswick Canada <sup>6</sup>  | Chilean<br>coastal<br>Batholith <sup>®</sup> The<br>Coastal<br>Cordillera of<br>Chile <sup>9</sup>   |  |
| Asia and others |   | Disko Bugt area,<br>West Greenland <sup>16</sup>  | Central<br>India<br>(1345±<br>22 Ma) <sup>10</sup>                        | Bayan<br>Obo,North<br>China (555-<br>420 Ma) <sup>11</sup>              | Bayan Obo, North<br>China (555-420 Ma)  |  |  |
| Europe          | Northern<br>Fennoscandia,<br>comprising<br>northern Sweden,<br>northern<br>Finland and<br>adjacent parts of<br>Norway and<br>Russia <sup>12</sup> | Kiruna<br>(Kiirunavaara<br>deposit)Northern<br>Sweden <sup>12, 22</sup>                 |   |   | Magnitogorsk<br>deposit, Russia <sup>23</sup><br>Porthleven,<br>Menheniot, Cornwall<br>and P - T sediments<br>(Western<br>Approaches) UK <sup>13</sup><br>Eastern Belgium <sup>14</sup> | Northeast<br>German<br>basin <sup>19</sup><br>Polish<br>Rotliegend<br>basin <sup>20</sup><br>Volcanics,<br>Gernsbach fault<br>zone <sup>21</sup><br>Streltsovka U<br>deposit<br>Russia <sup>24</sup> |  |
| Africa          |   | the eastern<br>Senegal <sup>15</sup><br>Phalaborw deposit<br>South Africa <sup>22</sup> |   | basalts at<br>Kibambale in<br>central<br>Shaba<br>(Zaire) <sup>17</sup> | Sandstones of<br>North Africa <sup>18</sup><br>Hercynian  | Hercynian of<br>North<br>Africa <sup>18</sup>  |  |

 Table 1 Global occurrences of albitisation through geological Time.

Information from: 1 Eilu et al. (2001), 2 Rubenach & Sayab (2004), 3 Clark et al. (2005), 4 Sun and Higgins (1996), 5 Hunt et al. (2005), 6 Van Staal et al. (2001), 7 Requia and Fontbote (2002), 8 Robert et al. (2002), 9 Hopper & Correa (2002), 10 Lamba and Agarkar (1988), 11 Smith and Wu (2002), 12 Carlon J (2002), 13 Gleeson et al. (2001), 14 Heijlen 2001, 15 Bassot (1997), 16 Kalsbeek (1992), 17 Kampunzu et al. (1993), 18 Hill et al. (2003), 19 Paulick & Breitkreuz (2005), 20 Pekala et al. (2003), 21 Brockamp et al. (1994), 22 Corriveau (2006), 23 Azovskova & Grabezhev (2008), 24 Chabiron et al. (2003)., Some of data (e.g. sediment and basalts) are the rock ages that albitisation affected; Most of data are albitisation ages (without description of rock types).

## 1.4.3 Albitisation Fluids

Albitisation on one hand depends on the composition and source of fluids and on the other on the composition of the affected rock types. The albitising fluids are predominantly hypersaline (50-60 wt% NaCl equivalent) and may contain CO<sub>2</sub> and/or CH<sub>4</sub> and N<sub>2</sub>. Depending on the maturity of the fluids, they can further be enriched in Mg, K, Fe, Cu and Au. However, salinity of albitising fluids may vary considerably (Table 2). The albitising process has the potential to generate mineralising fluids due to enrichment/removal of ore elements in the processes of fluid/rock reaction. During stages of mineralisations, the compositions of fluids are generally low-mid Na or poor Na (Table 2). Normally, albitisation occurred at high temperature (350–650°C) and

fluids mineralised at low temperature (130–350°C) except some IOCG mineralisation (Table 2).

| Albitisation   | Location or  | Mineralisation   | Types of  | Related  | Alteration   | Ore-stage   |
|--|--|--|---|--|--|---|
| /IOCG deposits   | district   | or albitisation  | albitisation  | alterations  | fluids   | fluids  |
| IOCG and<br>related<br>deposits <sup>1</sup>                         | The<br>Curnamona<br>province<br>and<br>Cloncurry<br>district,<br>Australia | age<br>1630-1580Ma<br>(Curnamona),<br>1540-1500Ma<br>(Cloncurry)             | Regional<br>scale<br>albitisation<br>systems            | Pre-date Na-<br>(Fe-Ca)-rich<br>assemblages,<br>Pre- to syn<br>mineralisation<br>K-Fe-Ca-Mg<br>alterations | 50-70% salt,<br>350-550°C,<br>CO <sub>2</sub> ±CH <sub>4</sub> ±N <sub>2</sub> -<br>Na (Ca, Mg)<br>rich. | Lower salt, 250-<br>350°C.<br>$CO_2\pm CH_4\pm N_2$ -K-<br>Fe (Ca, Mg) rich.                        |
| Cu-Au (-Mo) <sup>2</sup>   | Portia-<br>North<br>Portia,<br>Curnamona<br>Province                       | Albitisation-<br>1630Ma,<br>rocks-<br>1703±6Ma,<br>mineralisation-<br>1605Ma | Intense<br>albitisation<br>of the<br>meta-<br>sediments | Underlain<br>albite-<br>magnetite-<br>hematite<br>alteration   | H2O rich,<br>Low<br>metamorphic<br>Na-K-Ca-Fe?<br>400-450°C.   | Rich CO <sub>2</sub> -CH <sub>4</sub> -<br>HF-Oxidation   |
| IOCG (-Zn-<br>Ag) deposits <sup>3</sup>                              | Chilean<br>Coastal<br>Batholith,<br>South<br>America                       | (FeO between<br>116 and 114<br>Ma and<br>Copper-Gold<br>112Ma-110Ma          | Pervasive<br>distal<br>albitisation                     | Albite-<br>chlorite-<br>calcite-<br>hematite<br>alteration   | Hypersaline<br>CO <sub>2</sub> rich, 340-<br>470°C   | Saline fluid 29-<br>34% salt, 125-<br>175℃  |
| IOCG<br>systems <sup>4</sup>   | Panulcillo<br>and Teresa<br>de Colmo,<br>Chile                             | Lower<br>Cretaceous age  | Strong<br>pervasive<br>sodic<br>alteration,             | K-Na-Si-Fe<br>alteration<br>(Pannulcillo),<br>albite-chlorite<br>alteration<br>(Teresa de<br>Colmo)        | S- Fe, Cu, Au,<br>Na rich -<br>brines or<br>hypersaline.   | Metal-Na- rich<br>±K±Cl±Fe,<br>Volatile rich.<br>Lower T.   |
| Iron oxide<br>(Cu-U-Au-<br>REE)<br>deposits <sup>5</sup>             | The Salobo<br>IOCG<br>deposit<br>(Brazil)                                  | Archean<br>Salobo-pojuca<br>Group (rocks)                                    | Incipient<br>albitisation                               | Extensive<br>potassic<br>alteration  | 58 wt. %NaCl<br>equi, 360-<br>650°C  | 1-29wt.%NaCl<br>equi,CH4 <mol%,<br>133-270°C</mol%,<br>   |
| Base metal<br>(Cu-Zn-Pb-<br>Ag-Co)-Au<br>mineralisation <sup>6</sup> | North<br>Sweden,<br>Eurasia  | Lower<br>Proterozoic<br>succession   | Regional<br>and locally<br>albitisation                 | Complicated<br>Na-K-Ca-Si-<br>Fe alteration<br>assemblage  | High salinity,<br>rich in Na-K-<br>Ca.   | High salinity,<br>CO <sub>2</sub> -Cl, 210°C.   |
| Fe-REE-Nb<br>deposit <sup>7</sup>                                    | Northern<br>China  | Mineralisation-<br>555-420 Ma,<br>Proterozoic<br>sediments                   | Albitisation<br>in slates<br>and schists                | Fe-Na-K-F-<br>Ba alteration  | H2O-CO2-<br>NaCl, 1.3-<br>5wt. % NaCl<br>equi, 47-<br>66wt% XCO <sub>2</sub> .<br>246-362°C.             | Na-Ca-K-Fe-Mg-<br>Ba-F brines. 0-<br>60wt%<br>NaClequi.18-<br>66wt% XCO <sub>2</sub> .<br>129-500°C |
| Fe-Cu-Co-U<br>mineralisation <sup>8</sup>                            | Zambia in<br>central<br>Africa   | Cambrian age<br>Hook<br>Granitoid suite                                      | Unclear   | Unclear  | Unclear  | Unclear   |

Table 2 Examples of albitisation and related mineralisation, fluid compositions and conditions of mineralisation.

Data from: 1. Williams & Skirrow (2002), 2. Tan et al. (2004) and Teale et al. (2002), 3. Robert et al. (2002), 4. Hopper & Correa (2002), 5. Requia & Fontbote (2002), 6. Carlon (2002), 7. Smith & Wu (2002), 8. Nisbet (2002).

The composition of fluids depends on the sources or reservoirs and the interaction with various lithologies during fluid migration. Conventionally, the albitisation fluids are thought to be derived from multiple possible sources, e.g. formation/metamorphic water mixed with organic water  $\pm$  evolved meteoric and/or evolved seawater (Hunt et al. 2005); the evaporation of seawater + a seawater-meteoric water (Gleeson et al. 2001); crystallizing intrusions + other fluid sources and/or host rocks origin (Mark 2006); and mafic intrusions + magma reservoir (Angus &

Kanarissotiriou 1995). Warren (1997) suggested that the Proterozoic fluids were rich in  $HCO_3$  rather than NaCl as in modern evaporative systems. Thus, metamorphism/metasomatism fluids in Archaean and Proterozoic sediments were inferred to be Na +  $CO_2$  rich.

Albitisation fluids have an ability to produce supersaturated fluids (Putnis 2002). Albitisation fluids are frequently linked to microstructures and porosity (Tenailleau et al. 2006). However, precise processes of element remobilisation in variable albitisation gradients for mineralisation remain unclear e.g. in the Cloncurry districts and Yukon Canada Proterozoic basins. Specifically, the IOCG systems or Pb - Zn mineralization system are not quantitatively consistent with the pervasive intense albitisation in the Olary Domain.

#### 1.4.4 Enrichment / Depletion of Elements

Enrichment/depletion of elements during alteration results in changes of composition of the altered rock and changes in the fluid composition of the involved fluids. Consequently alteration like albitisation, may lead to secondary alterations, in this case from the resulting Fe-K-Ca-rich fluids. Enrichment/depletion of elements can be quantified by whole rock data following the method of Grant (1986). The definition of immobile elements is attained by petrologic observation and calculation from experiential immobile elements. For example, Eilu et al. (2001) described albitisation accompanying all processes of alteration surrounding the lode-gold bodies at Bronzewing, WA. Here the distal alteration assemblage is characterised by albitechlorite-calcite-ilmenite. Toward the intermediate assemblages, the accessory actinolite - epidote - titanite mineral phases gradually disappear. The intermediate alteration assemblage is albite - calcite - quartz - rutile - pyrite accompanied by accessory chlorite - ilmenite. At the same time, a muscovite - dolomite - ankerite - rutile assemblage has additional pyrite increases. The proximal alteration assemblage is muscovite + rutile + pyrite. The authors suggested that in this system Al and Ti were immobile elements. They then used the mass balance estimate to determine the gains/losses of elements during alteration. They further interpreted gains of Na-Sr-Y and losses of CO<sub>2</sub>, S, P, Au, Te, Ag, Bi, W, As, Rb, K and Sb. Oliver et al. (2004) suggested that Al, Ga ± Ti and Zr are nearly immobile during albitisation in the Eastern Mount Isa Block, Australia. Specifically, the Fe and K liberations are very clear in pelite (Snake CK), diorite (Ernest Henry), amphibolite (Eloise) and calc-silicate rock (Knobby) during albitisation.

Based on suggestions by Baumgartner & Olsen (1995), Clark et al. (2005) selected Al, Ti, Nb and Y, as the immobile elements during alteration in the Telechie Valley of the Olary Domain, Curnamona. Based on data sets from six samples, they inferred that albitisation and calcsilicate alteration formed at two stages of fluid flow. Mass balance/isocon calculations by Clark et al. (2005) suggested that the bulk volume examples experienced decreases of 12.7-26.2% during albitisation, accompanied by a mass loss of mainly SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, H<sub>2</sub>O, and to some extent Ba, Rb, Sr, and gain of Na2O in pelite, psammopelite and psammite during albitisation.

The mobility of Ca, Mg, Mn and P was thought to depend on the mineralogical composition of the respective rock types, gains of Cu, Zn and U and losses of Pb and Co were observed in psammopelite while in psammite a gain of Zn and a loss of Cu, U, Nb and immobile Pb were observed. In pelite a gain of U, Pb and Th and a loss of Cu and Zn were shown; (no data for Au available). Clark et al. (2005) also suggested that the losses of Ba, Sr and Rb were respectively linked to the progressive breakdown of K-

feldspar, plagioclase and biotite. Thus, the variability of element depletion is dependent on the relative abundances of each of these elements in the original rock.

The Al, Ti, Nb, Y are experimentally immobile elements but these elements may be entirely mobile as a group in metasediments during alteration. Single alteration margin in outcrop is the best selection for isocon to quantify the gains or losses of elements. Different intensity of albitisation has completely distinctive immobile elements. Different primary rock composition also controls/influences in change of immobile elements during alteration.

The siderophile elements were mostly removed during albitisation because their chemical characteristics are similar to Fe. The siderophile elements are: Cr, Mn, Fe, Co, Ni, Mo, Ru, Rh, Pd, Re, Os, Ir, Pt, Au, P, Ga and Ge (White 2006). According to Goldschmidt classification, lithophile elements are related to silicate phase; siderophile and chalcophile elements are respectively related to a metallic liquid phase and a sulphur liquid phase. Some of siderophile elements may also be chalcophile. Chalcophile can be siderophile while sulphur liquid is not available but aqueous fluid is. REE elements are siderophile. Frequently, REE elements are thought to be an example of entire mobility in geological events.

#### 1.4.5 Rare Earth Element (REE) Patterns

All REE can occur as  $3^+$  ions and are thus similarly charged. The REE variation is dependent on the ion radius. Ce and Eu have distinctly anomalous behaviour due to their occurrence as  $4^+$  and  $2^+$  species respectively.

Rare Earth Element distribution patterns have been widely applied to determine the origin of both rocks and minerals. Two REE patterns of rock/chondrite and mineral/chondrite (normalise REE data) are frequently used to interpret the REE composition of rocks and minerals (White 2006).

REE patterns of continental crust commonly show an enrichment of the light REE and a negative Eu anomaly. In contrast, MORB (Mid-Ocean Ridge Basalts) usually displays a light REE-depletion and a negative Eu anomaly. Conventionally, alkaline oxidised alterations mostly display a negative Eu anomaly but reduced mineralisation has a positive Eu anomaly linked to 2<sup>+</sup> Eu. For example, Castorina et al. (2006) suggested that albitised granites commonly have a negative Eu anomaly. Kaur et al. (2006) demonstrated that A-type granites in the Khetri copper belt have a negative Eu anomaly. For mineralisation, Lottermoser (1989) showed that the REE pattern of Ag-Pb-Zn sulphide bodies associated with the exhalites within the Willyama supergroup have a positive Eu value but a negative Eu anomaly in the Broken Hill lode.

Niiranen et al. (2005) presented the chondrite-normalised REE patterns of alteration and IOCG mineralisation (Fe-skarn), schist - marble, Serpentine Skarn – biotite-actinolite skarn, magnetite ore and altered gabbro. Again in this case, a negative Eu anomaly was found for alteration but positive Eu anomaly was found for mineralisation. The  $2^+$  Eu may be related to reduction and produce a positive anomaly.

Ward et al. (1992) examined the percent contribution of individual minerals, plagioclase, K-feldspar and tourmaline to REE patterns in granites by using the ratios of minerals/chondrite. Variation of REE patterns of minerals was found to be associated with sites of mineral grains, e.g. garnet for heavy REE enrichments (Ward et al. 1992; Kaur et al. 2006). The well-known Olympic Dam IOCG deposit is extremely enriched in REE from granite and mafic sources.

#### 1.5 Curnamona Geology

The Curnamona geology can be outlined on four aspects, stratigraphy, structural/tectonic evolution and metamorphism and magmatism. This summary is based on the recent integrations of previous work by Conor (2006; 2004), the 1:250000 sheet series by PIRSA and the 1:25000 lithologic maps (Laing, 1995).

#### 1.5.1 Stratigraphy

The Willyama Supergroup is divided into three groups; the Curnamona Group, the Saltbush Group and the Strathearn Group (see contents of Table 3 for stratigraphy). A demarcation of the groups is set between the bottom of the Bimba Formation of Saltbush Group and the top of Ethiudna Subgroup of Curnamona Group in the Olary Domain. The Curnamona Group is subdivided into the Ethiudna Subgroup and the Wiperaminga Subgroup marked imperfectly by the top of quartz-biotite metasediments and cross-bedded quartzites. The Ethiudna Subgroup consists of the psammitic Bewooloo Formation, equivalent to the more quartzitic/volcaniclastic Cathedral rock Formation, the albitic and calcalbitic metasedimentary Peryhumuck Formation and the fine grained quartz-mica schists of the Waukaloo Formation. The Wiperaminga Subgroup consists of the albitised George Mine Formation, the non-albitised metasedimentary Tommie Wattie Formation and the fine-grained quartz-biotite metasediments of the Mooleugore Formation equated to the Composite Gneiss and the Clevedale Migmatite in the Broken Hill Domain. The bottom of the Wiperaminga Subgroup is not explored remains uncertain (1720 Ma?). The rock units in the study area are (possibly George Mine Formation) part of the lowest units of the Curnamona Group.

## 1.5.2 Structural/Tectonic Evolution

The Structural/Tectonic Evolution of the field area comprises two deformation events: the highly metamorphosed – deformed Mesoproterozoic Olarian Orogeny (~1600-1500 Ma) (Conor 2006) and the Palaeozoic Delamerian Orogeny (500-450 Ma) (Conor 2006).

Three main Olarian deformations were the  $OD_1$ ,  $OD_2$  and  $OD_3$ . The  $OD_1$  is the earliest event expressed as a layer parallel foliation and isoclinal folds related to a possible early compression or expressing basin extension and continuous subsidence (Robertson et al. 1998; Conor 2004). The  $OD_2$  is established as tight to isoclinal recumbent folding, giving overturned limbs folding. The  $OD_3$  deformation resulted in open to locally tight folding around steeply plunging, NNE to E-trending axes associated with partial melting and emplacement of S-type granites. Shear zones mark an  $OD_4$  deformation along NE or E-W strikes (Conor 2004; Clark et al. 2005).

Two phases of deformation are recognized in the Delamerian Orogeny, likely at low to medium grade metamorphism which must have affected the underlying basement of Willyama Supergroup. The deformation is prominent in the Neoproterozoic cover units. The first phase ( $DD_1$ ) produced N-S shortening and northwest folding. The second phase ( $DD_2$ ) produced a slightly buckled foliation (cleavages of fold axes paralleling the general trend of the earlier  $OD_3$ ). The Delamerian tectonic movements also resulted in amplitude folding, the fault-bounded Weekeroo Inliers, N-S shorting, shear zone reaction and unconformity along NE, localised possible breccia formation and alterations.

Conor et al (2004) cited "Lithologies are best discussed in terms of metamorphic rock suites rather than separate petrographic types". The incentive for this was to outline albitisation gradients to indicate intensity and possibly directions of albitisation fluid flow.

## 1.5.3 Metamorphism

According to Conor (2006), metamorphism occurred during the period of 1600–1580 Ma. This approximates the age of Mundi Mundi Granite, and others in the Curnamona Craton. Metamorphic isograds are linked the metamorphic evolution of an anticlockwise/clockwise pressure-temperature-time (P–T-t) path or a possible late retro grade followed by a Delamerian metamorphism circle (Clarke et al. 1987; Webb& Crooks 2005. Conor 2006; 2004; Clark et al. 2005). Four metamorphic zones were recognised: i) Zone I - lower amphibolite facies, contains andalusite porphyroblasts (muscovite and chlorite), and increase of metamorphic grade from north to south; ii) Zone II metapelites / chloritoid-bearing schists (muscovite, chlorite and garnet) close to syntectonic granitoids; iii) Zone III lower granulite facies, pelitic rocks (kyanite and sillimanite or garnet perthitic feldspar, two-pyroxene mafic assemblages); iv) Zone IV - diagnostic phases, calcsilicate-bearing quartzofeldspathic rocks (calc-albitites). Metamorphism is further thought to be partly responsible for the formation of pegmatites in the study area (Conor 2006; Lu & Lottermoser 1997; Kent 2000).

Albitisation is part of metamorphism of the Curnamona province and links to other events (see Chapter 1.4.1). Two metamorphism high-grade events occurred between ca 1610 and 1585 Ma, and between ca 1570 and 1550 Ma (Rutherford et al. 2007). The first one approximates the age of the Ninnerie Supersuite granites (Conor 2006; 2004). Albitisation is throughout alteration in lower Willyama Supergroup with highly oxidised in Olary Domain and in the upper part with redox boundary. It may result from the dehydration, evaporitic and magmatic brines and then may result in other metamorphism events, e.g. K-Fe alteration and Fe alteration. The second one possibly associates with the shearing (and folding) and possible Au mineralisation and late U–Th–REE mineralisation

#### 1.5.4 Magmatism

Magmatism is expressed as at least five igneous suites in the Curnamona Province (Conor 2006): i) Basso Suite (~1720–1715 Ma) includes volcanics (Abminga Subsuite) and intrusives (Ameroo Subsuite)]; ii) 1693 $\pm$ 3 Ma Plumbago Formation (volcanics); iii) Lady Louise Suite (~1685 Ma, intrusives); iv) ~1650 Ma tuffaceous components of the Mooleulooloo Formation; and v)~1590–1580 Ma 'Ninnerie Supersuite', voluminous syn- to post-orogenic S-type-dominated granites. The three magmatic episodes (i), iii) and v)) in the Olary Domain (Conor 2006) compare to five identified magmatic events in the Broken Hill Domain. The Weekeroo amphibolite belongs to foliated type, its age equivalent to the Basso Suite (i.e. 1718–1715 Ma) (Conor 2006).

| Olary Block          |                                       | Broken Hill Block         |                                   | References                           |
|----------------------|---------------------------------------|---------------------------|-----------------------------------|--------------------------------------|
| Age (Ma)             | Stratigraphy                          | Age (Ma)                  | Stratigraphy                      |                                      |
| ~1600-~1580          | Dayanna Fm                            | Basin Invasion at 1610 Ma | Dalnit bore                       | Clark et al. 2005;                   |
| 1580 -1590           | Bimbowire suite                       |                           | metasediments Mundi-Mundi granite | Conor et al. 2004.                   |
| Na-Ca-Fe alteration  |                                       |                           |                                   |                                      |
| Na-Ca-Si alterations | Hydrothermal alterations              | $<1642 \pm 5$             |                                   | Skirrow 2000.                        |
| $(1582 \pm 22).$     | 1605 - 1610Ma and 1615 - 1635 Ma      |                           |                                   |                                      |
| 1651 ± 7             | Mooleulooloo Fm                       | <1655 ± 4                 | Bijerkerno                        |                                      |
|                      | (Psammopelite)                        |                           | metasediments                     |                                      |
|                      | Alconie Fm                            | <1672 ± 7                 | Cartwrights Metasediments         |                                      |
|                      |                                       |                           | King Gunnia Calcsilicate Member   |                                      |
| 1605 - 4             |                                       | 1605 - 0                  |                                   |                                      |
| $1685 \pm 4$         | Walparuta Fm<br>Lady Louise Suite (O) | $1685 \pm 3$              | Silver King Fm                    | Hores Gneiss (Extrusive)             |
|                      |                                       |                           |                                   |                                      |
|                      | Oonartra Creek Fm                     |                           | Fryers Metasediments              |                                      |
|                      |                                       | $1691 \pm 3$              | Allendale metasediments           |                                      |
| $1693 \pm 3$         | Plumbaga Fm                           | $1693 \pm 3$              | Parnell Fm                        | Intrusive                            |
| <1705-1693           | Bimba Fm                              |                           | Ettlewood Calcsilicate member     |                                      |
| ~1715 - 1705         | Basso Suite (O)                       |                           |                                   |                                      |
|                      | Ethiudna SB                           |                           | Himalaya Fm                       | Rasp ridge Gneiss $(1682 \pm 3)$     |
|                      | Tommie Wattie Fm                      |                           | Kyong Fm                          | Cues Fm Alders Tank Fm               |
|                      | & Mooleugore Fm                       |                           |                                   |                                      |
|                      | Quartzite Fm                          |                           | Lady Brassey Fm                   | Alma Gneiss $1704 \pm 3$ (Intrusive) |
|                      | George Mine Fm                        |                           | Thorndale Composite               | Mulculca Fm                          |
|                      |                                       |                           | Clevedale Migmatite               | Ednas Gneiss                         |
|                      |                                       |                           |                                   | Redan Gneiss                         |

 Table 3 Willyama Supergroup stratigraphy in the Curnamona.

Notes: 1. The Bimba formation is defined as the bottom of the Saltbush Group. 2. Basso Suite (1705 -1715 Ma) was not found in the Bimba formation. 3. The lithologies have possible gaps because the known thickness of Willyama Supergroup in the Weekeroo inliers (2-3 km) is much less than in Broken Hill Block (about 15 km).

#### **1.6 Project Aims**

This project aims at establishing reliable links between research and exploration for mineral resources using mapping of alteration gradients, whole rock and mineral geochemistry and thermodynamic modelling. The field area chosen for the project is a section of the Migmatite Creek area, Walparuta Inlier, Curnamona Craton containing units with pervasive, intense albitisation of most exposed rock types. This project aims to outline and characterise the intensity and variation of alteration that affected the various lithologies in the study area.

The objectives of this project are:

- to demonstrate gradients of intensities of albitisation and possible associated alteration assemblages;

- to demonstrate the mobilisation/fixation of major, trace and rare earth elements in variably albitised or altered (biotite alteration, calc-silicate alteration) whole rock samples of all lithologies present in the field area;

- to demonstrate sequential mobilisation of elements from individual mineral phases (e.g. feldspars, micas, amphiboles);

- to quantify mass and volume changes during albitisation / alteration using mass balance approaches (isocon construction);

- relative timing of alteration vs metamorphism, deformation events, pegmatites and granite intrusion.

## 2 APPROACH AND ANALYTICAL METHODS

The approach this project takes to meet its aims and objectives involves six steps:

- 1) Mapping of an area characterised by intense albitisation of different lithologies at variable intensities with the incentive to quantify this variation on a regional scale map and to determine the relationship of albitisation to lithologies, structural patterns and metamorphic or magmatic events. Sampling was carried out during the mapping.
- 2) Petrographic studies of lithologies and different degrees of albitisation/alteration and whole rock analysis to determine bulk chemical changes during the alteration event(s). A special emphasis is put on the variability of trace and rare earth elements.
- 3) Electron microprobe analysis of mineral phases to determine variation of major and trace element composition of individual mineral phases during albitisation/alteration,
- 4) Laser Ablation ICP-MS ultra trace element analysis to determine trace and rare earth element variation of individual mineral phases during albitisation/alteration.
- 5) Mass balance calculations to estimate the evolution of fluid compositions and quantify mobility of elements during albitisation/alteration.

## 2.1 Lithological and albitisation gradient mapping

This thematic mapping is an ideal approach to outline lithologies, structural features and mineralisation. Albitisation mapping focused on the spatial gradient of albitisation. Two maps were used for the preparation of albitisation mapping. They are the 1:50000 geological map of the Weekeroo Inliers and the 1:25000 lithological map of Outalpa. The lithological map was the base of the draft albitisation map. The sites of outcrops were marked on the draft map; meantime the data sets of GPS of points were recorded in the notebook with field description. The remote sensing image was applied as addition blank draft map replacing the traditional topography map from digital image with ArcGIS software. The intensity of albitisation was expressed in three grades: 0-45%, 45-65%, 65-100% albite in lithological units with visible albitisation for easy mapping. The form of albitisation boundaries are that albitisation zones can clearly be divided by field observation. Independent genetic lithologies were mapped including the pegmatites, amphibolites, breccias and quartz veins. The structures, antiforms, synforms and faults of different size were marked in the draft map. The sets of data of GPS were entered in the computer in X, Y and Z values and the points were automatically located on the ArcGIS map. The lithological boundaries were optimized by matching with the field map, photos and field records. The albitisation map was attained for determination of intensity of gradients.

## 2.2 Petrography

The petrography was described in the field by using hand lens and visible observation for quartz, feldspars, micas, magnetite and amphibole in different sizes and percentage in rock types. The thin and polished sections of samples were made by Pontifex and the petrography was carried out using a petrographic microscope in the Mawson laboratories. Opaque minerals were identified by reflected light microscope with magnification of 40-60 times. The lab microscopy can optimize the field determination and the results can be integrated to compare with whole rock data. Selected slides of samples were polished by Pontifex and grains of minerals were selected in photos of micrographs at 100-400 times for electron microprobe analysis and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LAICPMS) analysis for trace and REE elements of minerals. The selection criteria are that pairs of samples represent the alteration in outcrops and can cover petrography.

## 2.3 Whole rock analysis

## 2.3.1 X-Ray Fluorescence (XRF)

X–Ray Fluorescence (XRF) was used to determine the major and trace element content of samples of different types of rock. The instrument was a Philips PW 1480 X-ray Fluorescence Spectrometer, using an analysis program calibrated against several international and local Standard Reference Materials (SRMs). A dual-anode (Sc-Mo) X-ray tube was operated at 40kV, 75mA. For major elements, the oven-dried (100°C) powder of samples was fused at a temperature 950°C overnight. The single disc was melted for 6 - 15 minutes in a platinum crucible then poured in a heated mould and cooled quickly by compressed air. The resulting glass discs of samples contain 1 g of each powder sample and 4 g of Lithium borate flux. Major elements were analyzed in oxide form and iron was reported as  $Fe_2O_3$ .

For trace elements, three spoons of powdered samples (10–15 grams) were mixed with 6.5 ml of 2.5% Polyvinyl Alcohol solution and pressed into pellets at 5 atmosphere pressures. The dried pellets (room temperature) further were heated for 1-2 hours and subsequently were analyzed by the Philips PW 1480 XRF Spectrometer (see appendix B for details). Results were reported in ppm with 1 decimal place for less than 10 ppm concentrations.

## 2.3.2 Whole rock data including REE (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can be used to determine the rock chemical concentrations in ultra trace level for elements of interests. About 150 g of powder samples were prepared for whole rock analyses by Amdel. Samples were milled to about 150  $\mu$ m for easy solution by multi-acids. The 150  $\mu$ m size of powder was controlled by sample weight (<200 grams) each milling. Whole-rock data are analysed by Amdel method IC4 and IC3M. REE elements are determined by Amdel methods IC3R (for detail see appendix B).

## 2.4 Mineral analysis

## 2.4.1 Electron Microprobe Analysis

The Electron Microprobe Analysis allows determination of selected elements at level of percent or at about 100 ppm for minerals in samples. Points of analysis were selected on polished thin sections.

Polished sections are of size  $47 \times 25$  mm or  $75 \times 25$  mm, and 2.5 or 3 mm thick. The slides were prepared commercially in the size of  $47 \times 25$  mm and 3 mm thick. For analysis, samples were carbon coated (3 - 5nm).

The Electron microprobe analysis is based on the excited X-rays (X-ray spectrum and wavelength). The primary electron beam is accelerated to about  $1.5 \times 10^3$  eV (possible  $1-3 \times 10^3$  eV). The methods is non destructive.

Six slides were analysed at level of 100 ppm at the Adelaide Microscope Centre with a Cameca SX51 Microprobe with SAMx analysis and control software (Gresham Sirius EDS).

The Electron Microscope integrates two methods, the Energy dispersive X-ray Spectrometers (EDX) analysis and the Wavelength dispersive X-ray Spectrometers (WDX). The EDX produces the scanning results with a slow scanning mode and the fixed mode previews the possible point analysis results. The WDX analyses the selected points in minerals. Every point can be analysed at about size of 0.03 mm independently and a series of points can also be analysed along one line from a single mineral to another to get the changes of data in replacing reaction of minerals or their gradual reaction front.

The major elements and possible trace elements are selected as a package. The calibration of elements is linked to the reference of element content standard for each of analysed elements. The package was 15 elements: O, F, Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Sr and Ba. The results were presented as wt% of elements, A% (atomic number) and then calculated for the oxide forms automatically.

The selected minerals were plagioclase (albite to anorthite), K-feldspar, micas (biotite and muscovite), anthophyllite (Ferrigedrite). Furthermore, the results were used for the subsequent LAICPMS analysis for REE contents of mineral grains

#### 2.4.2 Laser Ablation ICPM analysis

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LAICPMS) was used to determine trace element contents in mineral grains. Durrant (1999) reviewed the achievements, problems and prospects of the technique about different laser wavelengths.

Inductively Coupled Plasma-Mass Spectrometry is the analysing parts of the LAICPMS method/technique at detection limits of ppm or ppb for most elements. The sample is presented to the high temperature (up to 10000K) plasma via laser ablation. The laser used is a New Wave Nd YAG (Y3Al5O12) 213 UV and directly ablates the solid samples.

The matrices of ions of atoms/molecules are passed through an interface cone to a vacuum; the beam is then focused into a quadrupole mass spectrometer (detector). Then the ions are classified by using their mass by the detector and a scanning electron multiplier. The ICP-Mass Spectrometer (Agilent 7500cs Semiconductor analyser) can be used to analyse both opaque and transparent materials alike.

Sample ablation and analysis involves two stages taking a total of about 95 seconds. The first stage of about 28 seconds is used to measure the background; the second stage of about 67 seconds analyses the Plasma produced by the laser ablation. Ar gas is used as a carrier with a passing speed of 15 L/Min at temperature of about 7500K.

Results from the ICP MS are converted using the GLITTER program (http://www.glitter-gemoc.com/.04/03/2008). Calculations of element concentrations are based on the Nist612 standard and normalised to chondrite. The trace element concentrations are determined relative to the known content of major elements as determined through electron microprobe analysis, for example, 9.00% of potassium for biotite and 11.50% of sodium for albite.

The spot size of laser ablation is about 30-50 microns in diameter; depth of ablation depends on the laser pulse parameter, the thermal conductivities and densities of minerals. The point of minerals must be carefully selected larger than the diameter of analysis to avoid the laser passing through the mineral and analysing other minerals or the underlying glass carrier slide. Thus, a decrease of the laser energy is useful for thin slides and small mineral grains.

The laser energy was selected from 80% to 40% to attain the appropriate energy level of 65%. The initial slide of sample ps008 was analysed at a level of 45% and the other 5 slides were at level of 65%. The parameters of the laser setup were 0.047mJ to 0.53mJ, 5Hz, 6.63-7.62 J/cm<sup>3</sup> in the operation processes and the diameter of points was selected at 30  $\mu$ m. The calculation of albite was respectively Na<sub>2</sub>O 11.5-12 wt% for slide Ps008 and Na exact value at ppm for others due to variable Na of albite. The calibration of minerals was 9 wt% K<sub>2</sub>O for biotite, 19-19.6 wt% Fe<sub>2</sub>O<sub>3</sub> for amphibole, 16 wt% K<sub>2</sub>O for K-feldspar. Two elements only can be selected to calculation for each slide. The additional Al<sub>2</sub>O<sub>3</sub> at 20.5 wt% and Al<sub>2</sub>O<sub>3</sub> 20 wt% were respectively calculation for albite and amphibole in slide Am011. The 7500 ICP MS is equipped with a cell of He collision for removal of matrix interferences of laser ablation instead of an Ar cell. 21 trace elements were analysed: REE (14 elements, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and the additional trace elements, Au, Cu, U, Co, Ni, Pb, Zn, Zr, Sr and Ba at level of ppm. The data sets were obtained and reported as:

GLITTER! - Trace element concentrations MDL filtered,

GLITTER! – 1 sigma error,

GLITTER! - Minimum detection limits (99% confidence) and

GLITTER! – Trace element concentrations normalised to chondrite.

All values are reported in ppm (http://www.glitter-gemoc.com).

#### 2.5 Mass balance calculations

The mobility of elements was determined following the Mass Balance estimate method outlined in Grant (1986). The quantification of compositional changes using this method critically relies on the determination of elements immobile during the alteration process. Selection of the immobile elements was based on chemical characteristics as determined through whole rock analysis as well as theoretical consideration of the mobility of elements based on their lithophile, siderophile or chalcophile character. However, even considered immobile elements (A1, Ti, Nb and Y, see Grant (1986)) in some instances were strongly removed during albitisation so that the group had no appropriate immobile element. The immobile elements were selected and optimized according to frequency of use in the literature database. They are A1, Ti, Y, Zr and Nb, Si, Ga, Sc, Ce and Nd in frequency order (Ohmoto & Lasaga 1982; Grant 1986; Davidson 1994; Baumgartner & Olsen 1995; Barnes 1997; Wibberley & McCaig 2000; Oliver et al. 2004). The immobile element groups were defined respectively for pairs of samples in albitisation zones by following the procedures of Grant (1986).

The approach of isocon based mass balance analysis, using whole-rock geochemistry, is used to quantify mass fluxes whereby the elemental concentrations of altered samples and unaltered precursors are plotted against each other. Elemental concentrations were arbitrarily scaled to aid in plotting, following Grant (1986). The relative mobility of elements depends on parameters such as types of rock, fluid compositions and P–T conditions during alteration. Immobile elements mean they have not been removed in samples of albitisation/alteration margin involved in fluid/rock reaction (Grant 1986; Baumgartner & Olsen 1995; Clark et al. 2006; 2005), the equation for the isocon line is expressed:

$$C^{A} = (M^{O}/M^{A})C^{O} = (\rho^{A}/\rho^{O}) C^{O}$$

where  $C^{O}$ ,  $M^{O}$  and  $\rho^{O}$  are respectively the element concentrations, mass and density in unaltered rocks and  $C^{A}$ ,  $M^{A}$  and  $\rho^{A}$  are the concentrations, mass and density of altered rocks. A best-fit isocon is based on the best definition of immobile elements by observations during alteration then calculated for each sample (Grant 1986). Following this, elements plotting in the fields above and below the isocon line represent element gains and losses in the samples from unaltered to altered rock.

For the determination of the immobile elements, the following tests are applied: 1) empirically selected immobile elements may be mobile;

2)  $\rho^A$  and  $\rho^O$  must be limited by the largest ranges of densities of the types of rocks from literature sources;

3) immobile elements have systematically similar values of  $C^A/C^O$  compared to the average of  $\rho^A/\rho^O$ . Porosities of rocks and changes of main mineral densities have to be considered.