Geochemistry of heavily altered Archean volcanic and volcaniclastic rocks of the Warrawoona Group, at Mt. Goldsworthy in the Pilbara Craton, Western Australia: Implications for alteration and origin

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The geochemical characteristics of Archean unusual siliceous rocks at Mt. Goldsworthy region in the Pilbara Craton were studied. The siliceous rocks have been assigned to the uppermost Warrawoona Group mafic volcanic rocks, and are overlain by quartz-rich sandstone units of the Strelley Pool Chert that probably represent continental margin sedimentation. The Warrawoona rocks have been heavily altered and are now composed dominantly of microcrystalline quartz, with subordinate mica, Fe-Ti oxides and unidentified silicates; original magmatic textures are only locally preserved. The complex alteration is assumed to result from multiple events including weathering during subaerial exposure, circulation of hydrothermal fluids, and metasomatic silicification. During alteration, Al, Ti, Zr, Th, Cr and Sc remained immobile, although their concentrations were lowered by a substantial increase in silica. Mutual ratios of these immobile elements such as Al2O3/TiO2, Cr/Th, Th/Sc, Cr/Al2O3 and Zr/TiO2 and comparison with the least-altered contemporaneous mafic-ultramafic rocks in the Pilbara Craton show that the altered rocks originated from high-MgO rocks such as komatiite and high-MgO basalt, possibly of Al-depleted type. The Mt. Goldsworthy rocks have significantly higher Th/Sc (0.024–0.1) values compared with primitive mantle values (0.005) and komatiite (0.01). This feature is interpreted as a result of crustal contamination, which is consistent with the early evolution of continental crust.

Keywords: Archean, Pilbara, altered mafic-ultramafic rocks, origin, geochemistry

INTRODUCTION

In this study, we discuss the origin of heavily altered Archean rocks distributed at southern margin of the Mt. Goldsworthy region in the northeastern Pilbara Craton, based on whole-rock major and trace element data including rare-earth elements, Zr, Th, Sc and Hf, and microanalyses of some constituent minerals. The rocks occur as a narrow basal unit that is assigned to the Warrawoona Group mafic volcanic rocks (Smithies, 2002) and are overlain with siliciclastic metasedimentary rocks that record an Archean shallow to subaerial sedimentary environment (Sugitani et al., 2003). The sedimentary succession has recently been assigned to the Strelley Pool Chert that represents Earth’s oldest continental margin sequence (Van Kranendonk et al., 2002). Thus the Warrawoona mafic rocks just below the Strelley Pool Chert at Mt. Goldsworthy are of special interest, in the context of early evolution of continental crust. Evolution of continental crust during the early Precambrian time has long been a major issue in the earth sciences (e.g., Taylor and McLennan, 1985; Condé, 1993; Gao and Wedepohl, 1995; Smithies et al., 2003; Smithies and Van Kranendonk, 2005). The early (>3.0 Ga) evolution of continental crust within the Pilbara Craton has been claimed, based on the record of erosion of ~3.5 Ga granitoid basement (Buick et al., 1995) and U-Pb zircon ages (McNaughton et al., 1993; Smithies et al., 1999; Thorpe et al., 1992). Trace element and isotopic signatures of the Warrawoona mafic to ultramafic volcanic rocks suggest the contamination of crustal materials (Green et al., 2000). In such circumstances, new data from Mt. Goldsworthy would potentially provide further evidence for early evolution of continental crust and related magmatic processes.
Chemical compositions of Archean greenstones have in most cases been modified to various degrees by metamorphism, alteration and weathering (e.g., Arndt et al., 1989; Arndt, 1994; Condie et al., 1977; Condie, 1981; Green et al., 2000; Gruau et al., 1992; Polat et al., 2002; Smith et al., 1980, 1984; Sun and Nesbitt, 1978; Tourpin et al., 1991; Van Kranendonk and Pirajno, 2004). In the case of the Mt. Goldsworthy rocks, their alteration was intense and they are now unusually siliceous rocks whose SiO₂ concentration is up to 90%; their original rock types have been inferred only from relict texture and Cr-Zr-Al-Ti systematics (Sugitani et al., 2003). Such heavily altered greenstones have generally been ruled out from most previous geochemical studies that were aimed at crustal evolution and magma genesis. However, in situations in which unaltered and relatively fresh samples are not available as is the situation at Mt. Goldsworthy, we cannot avoid studying heavily altered rocks. In this study we focus on high field strength and rare-earth elements (Zr, Th, Ti and REE), since these elements are generally resistant to post-magmatic events and are expected to provide important information about the origins and tectonic environments of altered Archean greenstones (e.g., Jochum et al., 1991; McCuaig et al., 1994; Polat et al., 1999; Xie et al., 1993).

**GEOLOGIC BACKGROUND AND SAMPLING**

According to the recent lithostratigraphic scheme for Archean granite-greenstone belts (Van Kranendonk et al., 2004), the Pilbara Supergroup in the eastern Pilbara Craton comprises four groups, namely the Warrawoona, the Kelly, the Sulfur Springs and the Gorge Creek Groups, in ascending stratigraphic order. Smithies (2002) interpreted the volcanic rocks at the southern margin of Mt. Goldsworthy and Mt. Grant as belonging to the Warrawoona Group. Geological interpretation (see Legend) of this area is after Smithies (2002), and is revised recently (see text). d: Representative stratigraphy of Mt. Goldsworthy volcanic-sedimentary succession (after Sugitani et al., 2003).

The Warrawoona volcanic rocks at the Mt. Goldsworthy are overlain by a sedimentary succession as noted earlier, which is correlated to the Strelley Pool Chert of the Kelly Group. The Strelley Pool Chert was first described in the Pilgangoora Belt, where it comprises a basal, quartz-rich sandstone with minor conglomerate, silicified laminated carbonates, mafic volcanics, and sedimentary rocks (chert and volcaniclastics). Hickman, 1983; Glikson and Hickman, 1981). The tectonic setting of eruption and the magmatic process producing the mafic to ultramafic rocks are controversial; for example, Barley (1993) concluded that the Warrawoona mafic-ultramafic volcanic rocks were formed in volcanic arc and near-arc settings, whereas Green et al. (2000) claimed that the rocks were erupted onto continental basement.

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<1.5 km thick basal komatiitic rocks and overlying ~5 km thick basaltic rocks (Van Kranendonk et al., 2002, 2004). The volcanism of the Euro Basalt from 3.35 to 3.32 Ga is interpreted to have occurred as continental flooding (Van Kranendonk and Pirajno, 2004 and references therein).

The majority of samples analyzed for this study were collected from the southwestern margin of Mt. Goldsworthy (15 samples), with additional samples from the stratigraphically correlative portion at Mt. Grant, 2 km west of Mt. Goldsworthy (2 samples; Fig. 1). At the Mt. Goldsworthy site, highly silicified, light gray to green, bright green and brownish yellow basal rocks occur. White, irregularly shaped quartz bodies of up to 1 m in length are found locally although cross cutting chert dykes are scarcely developed. The color of rocks at the outcrop is various, at least partially due to surface weathering. Near the top of this unit, light green, light gray and black cherts occur locally as small (<1 m-long) lenses or massive blocks of irregular shape. The relationship with the overlying silicilastic unit (the Strelley Pool Chert) is not always clear; however, local erosional contact is implied from abundant mafic to ultramafic clasts in the lowermost sandstones. At the Mt. Grant site, the basal massive rocks are less silicified and dark green, with reddish brown patches. In both Mt. Goldsworthy and Mt. Grant, no indicative structures such as pillow, layering and cumulate structures are observed.

PETROGRAPHY

Mt. Goldsworthy samples

The basal rocks at Mt. Goldsworthy are composed predominantly of quartz, with subordinate Fe-oxides, Ti-oxides and mica, and traces of carbonates and sulfides. The quartz grains are mostly microcrystalline (less than 10 µm in length) and locally mixed with larger grains (up to 500 µm). Fe-oxides and Ti-oxides occur as granules or flakes, and are often closely associated with each other. Micas are white, light bluish green, or brownish-yellow, and occur as masses or lamina-like aggregations, or as scattered flakes (Fig. 2a). Minute carbonate particles are occasionally found within relatively large quartz grains. Sulfide occurs mostly as relatively small (<10 µm) euhedral grains.

In spite of their relatively simple mineral assemblage described above, the Mt. Goldsworthy samples are characterized by a variety of textures. Some samples contain
Table 1. Chemical compositions of the basal rocks from Mt. Goldsworthy (GW) and Mt. Grant (VMGG)

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<th>Clastic</th>
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prismatic, lath-shaped and pseudo-hexagonal crystal pseudomorphs of polycrystalline quartz up to 2 mm in length (Fig. 2b), which are interlocked or closely packed with each other. They are in many cases outlined with slightly yellowish minute particles, which are assumed to be Ti-oxides. Skeletal rhomb- to hopper-shaped crystal pseudomorphs composed of Fe- and Ti-oxides (rutile and anatase) are also present. The pseudo-hexagonal, rhombic and skeletal habits of the pseudomorphs resemble pyroxene and olivine phenocrysts in mafic to ultramafic volcanic rocks (e.g., Nisbet et al., 1993; Orpen et al., 1993). They are dispersed in a quartz-rich matrix.

Closely packed lath-shaped pseudomorphs now composed of polycrystalline quartz resemble a cumulate texture (Figs. 2b and d for Mt. Grant sample; e.g., Arndt, 1994; Duchač and Hanor, 1987; Orpen et al., 1993). Interstices of these packed pseudomorphic grains are composed of brownish-yellow oxides that are probably mixture of Fe- and Ti-oxides. In addition to these crystallographic textures (see also figure 4 of Sugitani et al., 2003), a nodular texture is observed in one sample from Mt. Goldsworthy (Fig. 2c). Irregularly shaped nodule-like bodies are composed of polycrystalline quartz containing abundant minute oxide particles. The "nodules" contain rhomb- to cubic-shaped crystal ghosts. The matrix is enriched in oxides, although in some portions the relationship between nodules and matrix is transitional. Also some light grayish green rocks characterized by abundant lath-shaped pseudomorphs contain angular grains composed of microcrystalline quartz. The grains are more likely detrital, rather than crystallized. The rest of the samples do not show either magmatic or clastic textures.

### Mt. Grant samples

The Mt. Grant samples are characterized by a lower abundance of quartz and by enrichment of chlorite compared with those from Mt. Goldsworthy. Pseudomorphic minerals replaced by quartz are common. Particles of Fe- and Ti-oxides are also abundant in the rocks, and locally display textures of an anastomosing network. Rhombic

### Table 2. Results of EPMA analyses of mica and other aluminosilicates

<table>
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<tr>
<th></th>
<th>Point-1</th>
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<tr>
<td>SiO₂ (wt%)</td>
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<td>16.14</td>
<td>29.93</td>
<td>16.94</td>
<td>10.42</td>
<td>67.3</td>
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<td>54.2</td>
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<td>TiO₂</td>
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<td>0.07</td>
<td>0.08</td>
<td>0.09</td>
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<td>Al₂O₃</td>
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<td>17.54</td>
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<td>FeO</td>
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<td>28.25</td>
<td>44.17</td>
<td>53.01</td>
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<td>n.d.</td>
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<td>0.4</td>
<td>0.55</td>
<td>0.45</td>
<td>0.25</td>
<td>0.18</td>
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<td>Total</td>
<td>90.58</td>
<td>82.74</td>
<td>82.08</td>
<td>85.84</td>
<td>78.84</td>
<td>78.89</td>
<td>94.71</td>
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GW98-1-11

|          |         |         |         |         |         |         |         |         |         |
| SiO₂ (wt%) | 47.66   | 45.93   | 47.11   | 46.44   | 94.72   | 46.94   | 49.19   | 47.56   | 47.59   |
| Al₂O₃    | 33.81   | 32.89   | 33.93   | 32.33   | 2.77    | 33.53   | 33.76   | 33.28   | 33.58   |
| FeO      | 0.22    | 0.26    | 0.2     | 0.24    | 0.03    | 0.25    | 0.18    | 0.25    | 0.22    |
| MgO      | 0.6     | 0.52    | 0.53    | 0.65    | 0.07    | 0.56    | 0.74    | 0.68    | 0.67    |
| Na₂O     | 0.4     | 0.44    | 0.52    | 0.29    | 0.02    | 0.36    | 0.33    | 0.37    | 0.32    |
| K₂O      | 10.2    | 9.95    | 10.04   | 10.24   | 0.98    | 10.22   | 9.75    | 10.15   | 10.3    |
| BaO      | 0.05    | 0.06    | 0.03    | 0.08    | n.d.    | 0.08    | 0.03    | 0.14    | 0.12    |
| C₁₂O₁₈  | 3.22    | 2.87    | 3.1     | 2.64    | 0.22    | 2.97    | 2.74    | 3.01    | 3.13    |
| Total    | 96.17   | 92.91   | 95.46   | 92.92   | 98.83   | 94.91   | 96.73   | 95.45   | 95.93   |

VMGG2

|          |         |         |         |         |         |         |         |         |         |
| SiO₂ (wt%) | 24.75   | 24.68   | 24.33   | 23.84   | 23.88   | 29.11   | 25.78   | 25.2    | 28.59   |
| TiO₂     | 0.05    | 0.03    | 0.02    | 0.03    | 0.01    | 0.07    | 0.02    | 0.07    | 0.05    |
| FeO      | 31.47   | 30.54   | 31.1    | 31.39   | 31.77   | 26.53   | 29.04   | 29.87   | 25.16   |
| MgO      | 10.14   | 10.07   | 10.01   | 9.72    | 9.87    | 6.59    | 9.23    | 9.67    | 7.41    |
| Na₂O     | n.d.    | n.d.    | 0.03    | n.d.    | 0.01    | 0.03    | 0.06    | n.d.    | n.d.    |
| K₂O      | 0.02    | n.d.    | n.d.    | n.d.    | n.d.    | 0.41    | 0.16    | 0.06    | 0.01    |
| BaO      | 0.03    | 0.06    | 0.06    | 0.06    | 0.04    | 0.06    | 0.02    | n.d.    | 0.03    |
| C₁₂O₁₈  | 0.71    | 0.63    | 0.67    | 0.65    | 0.64    | 0.84    | 0.88    | 0.99    | 0.25    |
| Total    | 88.87   | 87.38   | 87.61   | 86.65   | 87.37   | 85.16   | 86.1    | 87.27   | 87.44   |
samples were decomposed twice by 9 ml HF/HClO4 acid. ICP-MS analyses was conducted as follows: 200~500 mg of powdered sample and flux (Li2B4O7) in the proportion of 1:5 (Sugisaki et al., 1977). The total concentrations of C, H and S were determined by INAA following the method of Shibata (1998). Chromium, Th, Sc, Hf, Sm, Eu, Yb, and Lu in all samples were measured by INAA following the method of Sugitani and Mimura (1977).

ANALYTICAL METHODS

Major elements were analyzed by an automatic X-ray fluorescence spectrometer (XRF) using fusion glasses made from a mixture of powdered sample and flux (Li2B4O7) in the proportion of 1:5 (Sugisaki et al., 1977). The total concentrations of C, H and S were determined using an elemental analyzer. The analyses of the minor elements (including rare-earth elements) were performed using XRF, a graphite-furnace atomic adsorption spectrometer (GFAA), an inductively coupled plasma mass spectrometer (ICP-MS) and instrumental neutron activation analysis (INAA).

Cobalt, Ni, Cu, Zn, Pb, Rb, Sr, Zr and Ba were analyzed by XRF; pressed discs containing a mixture of powdered sample and binder in the proportion of 2:3 were used, following the method of Sugitani and Mimura (1998). Chromium, Th, Sc, Hf, Sm, Eu, Yb, and Lu in all samples were measured by INAA following the method of Shibata et al., (2001). All rare-earth elements (REEs), and Y of selected samples were analyzed by ICP-MS. The preparation of sample solution for the REEs and Y for ICP-MS analyses was conducted as follows: 200~500 mg samples were decomposed twice by 9 ml HF/HClO4 acid (2:1 in v/v ratio) at 160°C, and subsequently evaporated to dryness. The residues were dissolved in about 2 ml of 1.7N-HCl and centrifuged at 12000 rpm for 10 min. The sample solutions were separated from the major elements using an AG50W-X8 cation exchange column. The solutions including REEs were evaporated to dryness and dissolved in about 15 g of 2%-nitric acid. This solution was subjected to ICP-MS analysis using 157 ppb In and Bi as internal standards. The analytical errors of the REEs estimated by determination of JB-1a, published by Geological Survey of Japan, were about 1~3%. The analytical results are listed in Table 1. Data of REE obtained by ICP-MS and those by INAA are nearly identical with each other, within 5% for La and Sm, and 10% for Yb and Lu.

In addition, some constituent minerals such as mica and other aluminosilicates were analyzed using an electron microprobe analyzer (EPMA), following the method of Enami et al. (2004). The analytical results are listed in Table 2.

RESULTS

Major elements of whole rock samples

The concentrations of the major elements of the Mt. Goldsworthy samples indicate that the chemical compositions of the Mt. Goldsworthy rocks are quite different from those of any other volcanic rocks (Table 1). The Mt. Goldsworthy rocks have high SiO2 concentrations (>80% for all but two samples), and the concentrations of TiO2 and Al2O3 range from 0.24 to 1.21% and from 1.41 to 6.55%, respectively. The Al2O3/TiO2 values range from 4.6 to 7.0. The concentration of Fe2O3 (total Fe as Fe2O3) and P2O5 vary widely from 0.05 to 18.6% and from 0.01 to 0.15%, respectively. Most samples are very low in MnO, MgO, CaO, and Na2O concentrations (<0.2%). The samples may be classified based on the K2O concentration: the K2O concentrations of half the samples are less than 0.05%, whereas the others exceed 0.4% (and are as high as 1.38%). The high-K samples tend to be poor in Fe (<0.05~0.08% as Fe2O3) in comparison with the low-K samples (1.79~18.67% as Fe2O3).

Compared with the Mt. Goldsworthy samples, the Mt. Grant basal rocks exhibit lower SiO2 (<70%) and higher TiO2, Al2O3, Fe2O3, MgO, P2O5, and H2O concentrations. The Al2O3/TiO2 values (5.8 and 5.1) are within the range of the Mt. Goldsworthy samples (4.6~7.0). The samples are characterized by very low concentrations of K2O (<0.05%), and high Fe2O3 (>18%).

Minor elements of whole rock samples

The Co, Ni, Cu, Zn, Pb, Sr, Ba, and Rb contents of the Mt. Goldsworthy samples are highly variable from sample to sample. Cobalt, Ni, Cu, Zn and Pb concentrations range from 2 to 29 ppm, from 12 to 154 ppm, from 7 to 124 ppm, from 7 to 98 ppm, and from <1 to 7 ppm, respectively. Sr and Ba concentrations also differ greatly, from <1 to 53 ppm, and from 70 to 871 ppm, respectively. Rb was detected (15~58 ppm) in only half of the samples showing high K2O concentrations.

The Zr, Cr, Th, Sc and Hf contents are less variable and vary within an order of magnitude. The Zr, Cr, Th, Sc and Hf concentrations are less variable and vary within an order of magnitude. The Zr, Cr, Th, Sc and Hf contents are less variable and vary within an order of magnitude. The Zr, Cr, Th, Sc and Hf concentrations are less variable and vary within an order of magnitude. The Zr, Cr, Th, Sc and Hf contents are less variable and vary within an order of magnitude. The Zr, Cr, Th, Sc and Hf concentrations are less variable and vary within an order of magnitude. The Zr, Cr, Th, Sc and Hf contents are less variable and vary within an order of magnitude.
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shows a distinct positive Ce-anomaly. The La/Yb ratios in all samples analyzed are from 1.3 to 23.5 (Table 1).

In common with the major elements excluding Si, the minor elements of the Mt. Grant samples tend to be present in higher concentrations than the Mt. Goldsworthy samples. However, the relative ratios of the high field strength elements (Zr, Th, Sc, Ti and REE), Cr, and Al are mostly within the corresponding ranges for Mt. Goldsworthy (Table 1).

Chemical composition of selected minerals

We analyzed 1) a yellowish-brown mixture of oxides in a relatively Fe-enriched sample (GW98-1-2; equivalent to the black portion in Fig. 2b), 2) a bluish-green mica in a K-rich sample (GW98-1-11; Fig. 2a), and 3) a dark green mineral in a less-altered sample (VMGG2; Fig. 2d). Their chemical compositions are listed in Table 2 and some interpretations are presented below.

1) The analytical results obtained for the yellowish-brown material show that they contain wide variations in SiO2, Al2O3 and FeO concentrations. Though rather variable, significantly high Cr2O3 contents are also observed, whereas the MgO, Na2O and K2O contents are quite low. The material appear to be not composed of any specific mineral, but rather of a mixture of alumino-silicates and Fe-oxides.

2) The bluish-green mica mineral is characterized by high K2O and Cr2O3 concentrations and thus identified as fuchsite. It contains trace amounts of Na2O and MgO. The high-K samples in addition to GW98-1-11 contain bright green to light blue patches and veins visible in hand specimens, which are thus probably fuchsite also.

3) The dark green mineral is optically identifiable as a chlorite group mineral, an observation supported by its chemical composition being characterized by high concentrations of MgO. It may also be noted that the mineral is characterized by relatively high Cr2O3 contents.

DISCUSSION

Recognition of immobile elements

As mentioned earlier, chemical compositions of Archean rocks have in most cases been modified to various degrees by metamorphism, alteration and weathering. This is also the case for the Mt. Goldsworthy rocks. The bulk chemical compositions of the rocks indicate that they are unusually siliceous for igneous rocks. Additionally, the presence of ubiquitous pseudomorphic minerals now composed of micro to granular quartz is diagnostic for silicification. In addition to silicification, other alteration events related to the formation of carbonate (carbonatization), chlorite (chloritization) and fuchsite (K-metasomatism) are inferred on petrographic and chemical grounds to have taken place, as discussed in detail in the later section.

In order to study the origin of heavily altered rocks like these, immobile elements represented by Zr and Ti could be a strong tool (Condie and Wronkiewicz, 1990; Cullers et al., 1993; Duchač and Hanor, 1987; Lowe, 1999), although it may be cautioned that under certain peculiar alteration conditions, even Zr and Ti can be mobilized (e.g., Salvi and Williams-Jones, 1996). Concern-
ing the Mt. Goldsworthy altered rocks, the elements such as Zr, Ti, Sc, Th and Al are indeed immobile, because they correlate positively with one another (r > 0.75) (Table 3). Their inverse correlation with SiO$_2$ (r = –0.75), on the other hand, suggests silica addition during alteration. However, this silica addition was not accompanied by substantial remobilization of these "immobile" elements. Consequently, their mutual ratios could be used as a discriminator when studying the origin of the Mt. Goldsworthy rocks.

Compared with these "immobile" elements showing high mutual correlation coefficients, Cr and REEs need more careful consideration. The lower correlation coefficient of Cr with other "immobile" elements suggests its redistribution during alteration events. Among the three rare-earth elements in Table 3, Yb tends to show the highest positive correlation with elements such as Zr, Ti and Al, whereas La exhibits the lowest. The behavior of Cr, La, Sm, and Yb during alteration will be discussed in the later section.

**Origins of the Mt. Goldsworthy basal altered rocks**

Sugitani et al. (2003) suggested that the basal rocks at Mt. Goldsworthy were originally of mafic to ultramafic composition, based on the distribution patterns discernible in a Zr/TiO$_2$-Cr/Al$_2$O$_3$ diagram. The data newly acquired in this study also plot in the same area (Fig. 4). The uncertainties in Cr behavior during alteration do not require revision of this conclusion, as on this diagram the discrimination of mafic and ultramafic rocks from more felsic rocks depends largely on Zr/TiO$_2$ ratio that is conservative during alteration as discussed above. In Table 4, the average values and ranges of Th/Sc, Cr/Th and Cr/Zr ratios of the samples analyzed here and representative values for Archean igneous rocks (Condie and Wronkiewicz, 1990; Condie, 1993) are shown together. A Cr-free indicator, the Th/Sc ratio, is lower than 0.05 in most samples (Table 1), close to the basaltic value (0.02). Though not so sensitive as Th/Sc, the Al$_2$O$_3$/TiO$_2$ values also could be used as an indicator of the original rock type (e.g., Sugitani et al., 1996). Archean data compiled by Sugitani (2000) show that while some mafic to ultramafic rocks have Al$_2$O$_3$/TiO$_2$ values lower than 10, intermediate and felsic rocks always have Al$_2$O$_3$/TiO$_2$ values higher than 10. The Al$_2$O$_3$/TiO$_2$ values of the Mt. Goldsworthy rocks are commonly lower than 10 (Table 1). These lines of evidence convincingly suggest an original mafic to ultramafic composition of the basal rocks and furthermore suggest that Cr can be regarded basically as immobile like Zr, because values of indicators using Cr content such as Cr/Th and Cr/Zr are consistent with those of other Cr-free indicators such as Th/Sc, Zr/TiO$_2$ and Al$_2$O$_3$/TiO$_2$ (Tables 1 and 4). It is inferred from these facts that Cr-redistribution during alteration was not significant. Chromium incorporated in primary minerals such as pyroxene and Cr-spinel appears to have been released during decomposition of host minerals and then re-incorporated into secondary minerals such as fuchsite and other aluminosilicates (Table 2), probably at the scale of a hand-specimen.

| Table 3. Correlation coefficients between HFSEs, Cr, Al, and SiO$_2$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| TiO$_2$         | Al$_2$O$_3$     | Zr              | Cr              | Th              |
| TiO$_2$         | 1  | 0.96 | 0.96 | 0.53 | 0.83 | 0.86 | -0.77 | 0.53 | 0.73 | 0.81 |
| Al$_2$O$_3$     | 1  | 0.97 | 0.46 | 0.89 | 0.87 | -0.85 | 0.46 | 0.74 | 0.87 |
| Zr              | 1  | 0.45 | 0.84 | 0.86 | -0.86 | 0.49 | 0.79 | 0.92 |
| Cr              | 0.33 | 0.64 | -0.31 | 0.10 | 0.26 | 0.49 |
| Th              | 1  | 0.76 | -0.76 | 0.38 | 0.58 | 0.70 |
| Sc              | 1  | 0.86 | 0.28 | 0.62 | 0.79 |
| SiO$_2$         | 1  | -0.32 | 0.69 | -0.83 |
| La              | 1  | 0.82 |
| Sm              | 1  | 0.82 |
| Yb              | 1  |

| Table 4. Th/Sc, Cr/Th and Cr/Zr for Archean Igneous series and Mt. Goldsworthy rocks |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|
| Granite                          | Tonalite        | Felsic V.       | Andesite        | Basalt          |
| Th/Sc                            | 10  | 1.3 | 0.13 | 0.15 | 0.02 | 0.0035 | 0.02 | 0.1 |
| Cr/Th                            | 0.2 | 6.5 | 12.5 | 67  | 500  | > 10000 | 13000-4800 |
| Cr/Zr                            | 0.04 | 0.3 | 0.12 | 1.4 | 5.5  | > 75  | 14-51 |
| Mt. Goldsworthy                  |                |                |                |                |

Note: Data for average values of igneous rocks are quoted from Condie and Wronkiewicz (1990) and Condie (1993).

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It may be additionally noted that there are no observed systematic differences in geochemistry between the samples showing different petrographic features. The samples without igneous textures have Zr/TiO₂ and Th/Sc values of 72.6 to 100 and 0.024 to 0.1, respectively, which cannot be discriminated from the values of the igneous-textured samples (75–104 for Zr/TiO₂ and 0.029–0.076 for Th/Sc) (Table 1). Some of these samples occasionally have clastic textures as described in the former section, implying that they represent a volcaniclastic portion. The rest of the samples without either clastic or magmatic textures may have originated from fine ash of the same composition.

**Correlation with Pilbara volcanic formations and assumed original rock type**

Based on the assumption that the Mt. Goldsworthy basal rocks were originally mafic to ultramafic rocks, we compare them here with Archean basaltic-komatiitic formations in the Pilbara Craton. The Pilbara basaltic-komatiitic formations comprise tholeiitic basalt (THB), tholeiitic gabbro (THG), peridotitic komatiite (PK), high-magnesian basalt (HMB) and high-alumina basalt (HAB), which can be discriminated on a Zr/TiO₂-Cr/Al₂O₃ diagram (Fig. 5). Though partially overlapping with each other, high-MgO rocks such as HMB and PK tend to have higher values of Cr/Al₂O₃ than the other types (THB, THG, and HAB). In this diagram, all of the Mt. Goldsworthy samples as well as Mt. Grant least altered samples plot within the high-MgO field, irrespective of random sampling and various lithology. It is thus unlikely that the distribution of samples in the high Cr/Al₂O₃ field resulted from Cr-redistribution and silicification. Suspected Cr-redistribution mentioned in the earlier section could be negligible in discriminating original rock type on this diagram. Consequently we infer that the heavily altered rocks were originally komatiites or high-magnesian basalts.

Though the original rock type can be assumed as discussed above, exact chemical compositions of the Mt. Goldsworthy are almost impossible to infer, due to intense alteration. High-MgO rocks in general contain >10% MgO; however MgO concentrations of the Mt. Goldsworthy rocks are mostly less than 1%. Even the least altered, relatively Mg-enriched samples from Mt. Grant site have MgO concentrations less than 5%. These features are explained by removal of Mg during alteration. Additional removal of Fe and Ca is indicated from the presence of samples with markedly low Fe₂O₃/TiO₂ (<1) and CaO/TiO₂ (<0.3). Silica-enrichment of the Mt. Goldsworthy rocks is not solely attributed to removal of these mobile elements and retention of Si. As suggested by inverse relationships of immobile elements with Si, Si has been substantially added. Such intense alteration of Mt. Goldsworthy rocks makes it difficult to identify their original chemical composition. Nevertheless, the following conclusion could be made. Mt. Goldsworthy rocks are characterized by low Al₂O₃/TiO₂ values (4.6–7). The low Al₂O₃/TiO₂ values are attributed mainly to an original low concentration of Al₂O₃; even the least altered samples with SiO₂ around 65% contain less than 9% Al₂O₃. Therefore the Mt. Goldsworthy rocks may have been originally Al-depleted, in addition to MgO-enriched.

**Igneous petrogenesis with implications of REE behavior**

Green et al. (2000) suggested that the parental magma of the mafic-ultramafic volcanic rocks in the Warrawoona Group had been contaminated with crustal material (up to 25%). Such a crustal contamination model is motivated by the fact that significant depletion in mantle-derived elements such as Nb is associated with increased crustal components such as Th, LREE, and U (Arndt and Jenner, 1986; Cattel, 1987; Cattel and Arndt, 1987; Jochum et al., 1991; Sun et al., 1989; Rudnick and Fountain, 1995). This crustal contamination model for the Warrawoona rocks may explain the observed significant variations in trace element ratios such as La/Yb, La/Sr and Th/Sr of the Mt. Goldsworthy rocks (Fig. 3 and Table 4).

In order to test this model, we introduce here La-Sm-Yb-Th-Sc systematics, where the Th/Sr ratio is used as...
an indicator for crustal contamination, based on the Archean upper crust (Th = 5.7 ppm, Sc = 14 ppm) having a Th/Sc ratio (0.41) distinct from primitive mantle (Th = 0.064 ppm, Sc = 13 ppm) (Th/Sc = 0.005) (Taylor and McLennan, 1985) and komatiite (Th = 0.3 ppm, Sc = 28 ppm) (Th/Sc = 0.01) (Condie, 1993). In both Th/Sc-La/Yb and Th/Sc-La/Sm plots, the Mt. Goldsworthy rocks roughly define positive trends, consistent with the trend for high MgO rocks in the Warrawoona Group (unpublished data) (Fig. 6). Consequently, the observed La/Yb and La/Sm variations may be simply interpreted by crustal contamination, assuming the Th/Sc ratio, sensitive to crustal contamination, is conservative during alteration. However, the results of mixing calculations using komatiite data as an end-member for parental high-MgO magma evoke caution (Fig. 7), because half of the Mt. Goldsworthy rocks are inconsistent with any of the mixing lines using three different felsic end-members; Archean Upper Crust, TTG (tonalite-trondhjemite-granodiorite) and granite. This feature can be explained by La-redistribution during alteration and resultant perturbation of La/Yb ratio, because correlation coefficients between Th, Sc and Yb ($r = 0.76$ for Th-Sc and $r = 7.0$ for Th-Yb) are significantly higher than those between Th, La and Yb ($r = 0.40$ for La-Yb and $r = 0.38$ for La-Th) (Table 3). Several authors also reported that during alteration of Archean greenstones, the LREE contents have often been modified, whereas the HREE compositions are less affected (Arndt et al., 1989; Condie et al., 1977; Tourpin et al., 1991; Polat and Hofmann, 2003; Hayashi et al., 2004). Due to the modification of La/Yb ratios documented above, it is equivocal which line in Fig. 7 is the most likely for the mixing trend; however some samples of the Mt. Goldsworthy appear to be significantly contaminated (>10%) with crustal materials of felsic composition.

**Implications for alteration processes**

As previously mentioned, the Mt. Goldsworthy rocks had been subjected to multiple alteration events; in addition to silicification, other alteration events related to the formation of carbonate (carbonatization), chlorite (chloritization) and fuchsite (K-metasomatism) are inferred. The previous presence of carbonate minerals is

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overlying Strelley Pool Chert, closely related to the erup-
tion is thought to post-date the deposition of the
Kranendonk and Pirajno, 2004). According to the authors,
rocks are assigned, has been studied for samples collected
Warrawoona volcanic rocks, to which the heavily altered
as a heat source. Alteration of the upper succession of
submarine caldera setting and intruding granitoid plutons
whereas V an Kranendonk and Pirajno (2004) suggested
ridge type hydrothermal circulation (mantle-source),
and Nakamura and Kato (2004) emphasized the mid-ocean
heat source is still controversial; Kitajima
Warrawoona mafic to ultramafic volcanic rocks well-ex-
ploited seafloor hydrothermal circulation is responsible for the alteration of these
Warrawoona volcanic rocks, although tectonic setting and
heat source is still controversial; Kitajima et al. (2001) and
Nakamura and Kato (2004) emphasized the mid-ocean
ridge type hydrothermal circulation (mantle-source),
whereas Van Kranendonk and Pirajno (2004) suggested
submarine caldera setting and intruding granitoid plutons
as a heat source. Alteration of the upper succession of
Warrawoona volcanic rocks, to which the heavily altered
rocks are assigned, has been studied for samples collected
from the North Pole Dome and the neighbouring area (Van
Kranendonk and Pirajno, 2004). According to the authors,
the alteration is thought to post-date the deposition of the
overlying Strelley Pool Chert, closely related to the erup-
tion of the overlying Euro Basalt. In addition, the reported
high K$_2$O signature of basalts beneath the Strelley Pool
Chert was attributed possibly to weathering process dur-
ing subaerial exposure (Van Kranendonk and Pirajno,
2004 and references therein).

At Mt. Goldsworthy-Mt. Grant, the Euro Basalt is only
distributed locally outside the map in Fig. 1. Thus, al-
teration related to the Euro Basalt is unclear, although
the following points can be emphasized: 1) Chert dyke
swarms, well developed at North Pole area, cannot be
seen. 2) The Strelley Pool Chert sediments were pervasive-
silicified, whereas silicification of the underlying
Warrawoona volcanic and volcanic rocks may have been
restricted around the uppermost portion of a few tens
meters, assuming that their present distribution at out-
crop reflects resistance against weathering. 3) The vol-
canic and volcaniclastic rocks may have been sub-aeri-
ally exposed and weathered, as inferred from local ero-
sional contact. 4) Eruption of the volcanic rocks prob-
ably occurred at a continental setting.

Apparently, the alteration process and mechanism at
Mt. Goldsworthy region are not equivalent to well-docu-
mented seafloor hydrothermal alteration of the middle to
lower Warrawoona rocks. Alteration of Mt. Goldsworthy
rocks may have been a result of complex process includ-
ing weathering and interaction with seawater at relatively
low temperature, in addition to hydrothermal alteration,
although the whole picture is still unclear.

**CONCLUSIONS**

The basal rocks at Mt. Goldsworthy region, which are
assigned to the uppermost Warrawoona Group of the
Pilbara Supergroup in the eastern Pilbara Craton, are com-
posed mostly of microcrystalline quartz, iron oxides, and
secondary alumino-silicates. Although they partly display
magmatic textures, their chemical compositions are quite
different from those of igneous rocks; SiO$_2$ concentra-
tions of most samples except two exceed 80%. The rocks
have been subjected to several different alteration events
such as carbonatization, chloritization, K-metasomatism
and silicification. The alteration is assumed to result from
weathering during subaerial exposure after eruption, cir-
culation of hydrothermal fluids and metasomatic
silicification.

Despite significant modifications of their composi-
tions, the original rock types can be revealed using the
relative ratios of Al, Ti, Zr, Th, Cr and Sc, which are con-
servative during alteration. Geochemical indicators such
as Al$_2$O$_3$/TiO$_2$, Zr/TiO$_2$, Cr/Al$_2$O$_3$, and Cr/Th all show that
the Mt. Goldsworthy rocks were originally of mafic to
ultramafic composition. Comparisons with data from the
Pilbara basaltic formations also suggest original high-
MgO compositions (i.e., komatiite, high-MgO basalt) and
possibly Al-depletion. La-Sm-Yb-Th-Sr systematics also
imply crustal contamination of the parental magma, which
is consistent with the assumed depositional environment
of the overlying Strelley Pool Chert and the early develop-
ment of the continental crust.

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