THE ALUMINIUM SATURATION INDEX AND THE MgO/TiO2 RATIO:
TWO PARAMETERS INFLUENCED BY P H2O AND THEIR USE TO
DISCRIMINATE MAGMA SERIES

ESSAID BILAL* AND ANDRÉ GIRET**

ABSTRACT The Aluminium Saturation Index is related to the MgO/TiO2 ratio and both may be added to other typological parameters commonly used in the granitic series discrimination. Some well-known examples are listed and they lead to propose new geochemical limits characterizing different geodynamic settings: 1: calc-alkaline granitoids (high Ca and low K) together with the island arc tholeiitic granitoids (ASI=1 for MgO=1.8% and MgO/TiO2 =2); 2: crustal peraluminous granitoids (ASI>1 and MgO/TiO2 = 3) produced in the collision zones; 3: tardi- and post-collision (K calc-alkaline) granitoids (ASI=1 for MgO=3.7% and MgO/TiO2 =4) and 4: the alkaline and peralkaline granitoids and the mid-ocean ridge tholeitic granitoids emplaced in rifting or doming zones (ASI=1 for MgO=0.8% and MgO/TiO2=1).

Keywords: granitoid, peraluminous, calc-alkaline, peralkaline, geodynamic settings, ASI, MgO/TiO2

INTRODUCTION Tuttle & Bowen's (1958) experiments in the system Na2SiO3-SiO2-H2O and Vodder's ones (1965, 1969) in the system diopside-anorthite-H2O emphasized the role of P H2O on magmatic crystallization. Presently, two types of cumulates have been observed. The first one, corresponding to a high P H2O, produces basic-ultrabasic rocks, whereas the second one, corresponding to low P H2O, produces anorthositic rocks. These two trends may be related to the well-known evolution paths, respectively in the oceanic suites (basal- ultrabasic) and in the continental suites (anorthositic). Further studies (Bessen & Fonteilles 1974, Sisson & Groves 1993, Katamoto 1997) also confirmed the importance of P H2O irrespective of geodynamic background, such as tholeiitic and calc-alkaline orogenic magmatism. Most of the above studies have been carried on volcanic series.

The topic of this paper is to analyze the effect of the water content on two granitic discriminant parameters, the aluminium saturation index (ASI) and the MgO/TiO2 ratio. Several authors have used the ASI to classify the granitic rocks (Shand 1949, Debon & Le Fort 1983). In the following, the ASI will be associated to MgO and TiO2, which may be both, considered as representative of the degree of differentiation in the granitic series. Since, these three elements remain mainly unaffected by the tardi- and post-magmatic alteration. Therefore, the MgO/TiO2 ratio has also been proposed for the characterization of granitic suites (Bilal 1991, Bilal & Fonteilles 1991).

Considering the existence of different, and sometimes confusing vocabularies, the paper will refer (Table 1) only to the Barbara's (1990) synthetic terminology.

P H2O AND ASI RELATIONSHIPS In granitoids, the Al-saturation value corresponds to the Al which is left after the calculation of CIPW normative feldspars, considering that the Ca apatite content enters the anorthite. Then, the ASI is reflected by the atomic ratio Al/(Na+K+2(Ca-3P/3)). During the evolution of different magmatic magmas, the ASI ratio varies according firstly to the mineralogical assemblages, and secondly to the composition of different mineral phases. The first ASI variation type is illustrated by the different Al-saturation value from one mineral to the other: 0.3 to 0.5 in the amphibole, 1 in feldspars, 1 to 1.5 in the biotite, and 2 to 2.5 in the muscovite. The second ASI variation type may be understood with the biotite, in which the Al also varies according to the crystallographic structure (Nockolds 1947). The liquid evolution is related to the ASI of the crystalizing minerals. For example, following the feldspar fractionation in which the ASI=1, an Al-undersaturated liquid will be Al- impoverished whereas an Al-saturated liquid will be Al-enriched (Zen 1986). In a metaluminous magma, the feldspar fractionation, as: feldspar cumulates, will not significantly change the Al content of the residual liquid. Illustrative petrological examples may be adduced, as: (1) in the plutonic alkaline series of the Niger (Le"ger 1980, Moreau 1982), where plagioclase cumulates control the ASI decrease of the residual liquid (Fig. 1A); (2) as in the plutonic suites of Kenya (Giret 1983), where the fractional crystallization of Ca-Fe-Mg-minerals and plagioclase lead to a regular ASI increase of the residual liquid.

Besides feldspar, the biotite is another aluminous mineral phase (ASI=1) whose crystallization also affects the magma evolutionary path. Therefore, in Al-saturated systems, with respect to quartz and

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Table 1 - The list of examples taken into account.

<table>
<thead>
<tr>
<th>Type</th>
<th>Tectonic setting</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA</td>
<td>Collision or post collision zones</td>
<td>Suite</td>
</tr>
<tr>
<td>CCA</td>
<td>Collision or post collision zones</td>
<td>Orogenic</td>
</tr>
<tr>
<td>HLO</td>
<td>Subduction zones</td>
<td>Suite</td>
</tr>
<tr>
<td>TOR</td>
<td>Rifting or doming</td>
<td>Anorogenic</td>
</tr>
</tbody>
</table>

C: crustal; ST: shearing and thrusting; CA: collision autochthons; CI: collision intrusive; H: hybrid; LO: late orogen; IA: island arc; OR: ocean ridge; A: alkaline.
PH2O AND MgO/TK>2 RELATIONSHIP

At constant pressure, MgO and TiO2 contents are closely dependent on temperature and are both related to the differentiation degree of a magmatic suite. Mg and Ti are abundant in the Fe-Mg silicates and in the Fe-Ti oxides. Moreover, in the granitoids, the Ti content of biotite depends on the Ti content of the magma, the lower Ti-saturation boundary being constrained by the equilibrium with amphibole.

The crystallization of Fe-Mg silicates and of Fe-Ti oxides depends on the oxygen fugacity which is related to P(H2O) (Presnall 1966, Presnall et al. 1978), in an equilibrium $\frac{1}{2}H_2 + Fe^{3+} + O^{2-} \rightleftharpoons Fe^{2+} + OH^-$.

Numerous experiments on basalts (Yoder 1965, Yoder 1969, Sekine & Wyllie 1983, Sisson & Grove 1993) support the increase of the spinel stability field to the detriment of the silicates ones when water is added to the system. In a same way, according to the Moon Al-basalt melting experiments performed by Ford et al. (1972), the stability field of the spinel extends to the liquidus under low pressure (2 kbar) and wet conditions. On the other hand, under dry conditions the spinel does not appear at the liquidus but under high pressure (10 kbar). Therefore, the crystallization sequence of the Fe-Mg silicates and of the Fe-Ti spinels is closely related to P(H2O). Consequently, in mid and more evolved magmatic suites, the MgO/TiO2 ratio will be related to P(H2O) too.

In the volcanic tholeiitic series, the iron enrichment is a result of the reducing conditions (Kuno 1950, Osborn 1959). In such magmas, the low water pressure forbids the crystallization of quartz and biotite, even under low temperature. On the other hand, in the volcanic calc-alkaline series, the evolution is constrained by oxidizing conditions in a water-rich environment (H2O from 4 to 6 wt. %). In this case, as the magnetite crystallizes during the evolution of the magma, the P(H2O) keeps up its high values, which fits the quartz and biotite stability even under low temperature. Such conditions result in different MgO/TiO2 ratios, in the intermediate and evolved rocks Japanese calc-alkaline volcanic series MgO/TiO2=2 (Fonteilles 1976) while in the Japanese tholeiitic series MgO/TiO2=1.5.

In the anorogenic suites, the differentiation of the calc-alkaline basalts occurs under reducing and low P(H2O) conditions (Upton &
Table 2 - A summary of our results: ASI, MgO/TiO₂, and geodynamic environments (Figs. 1 and 2)

<table>
<thead>
<tr>
<th>Origin</th>
<th>Granitoid types</th>
<th>Type</th>
<th>ASI</th>
<th>MgO/TiO₂</th>
<th>Tectonic setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crustal</td>
<td>Intrusive Two-mica Leucogranites</td>
<td>C₂T</td>
<td>ASI &gt;1.1</td>
<td>3 ± 0.2</td>
<td>Collision</td>
</tr>
<tr>
<td>Peraluminous rocks</td>
<td>Peraluminous Autochtonous Granitoids</td>
<td>C₃A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peraluminous Intrusive Granitoids</td>
<td>C₃I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed origin (Crust+Mantle)</td>
<td>Calc-Alkaline Granitoids (High K-Low Ca)</td>
<td>H₅O</td>
<td>ASI = 1</td>
<td>MgO = 3.7%</td>
<td>Post-collision zones</td>
</tr>
<tr>
<td>Metaluminous or Calc-alkaline</td>
<td>Calc-Alkaline Granitoids (Low K-High Ca)</td>
<td>H₅A</td>
<td>ASI &gt;1</td>
<td>MgO = 1.9%</td>
<td>Subduction zones</td>
</tr>
<tr>
<td>Tholeitic Alkaline Peralkaline</td>
<td>Island Arc Tholeitic Granitoids</td>
<td>T₄A</td>
<td>ASI = 1</td>
<td>MgO = 0.8%</td>
<td>Rifting or doming Zones</td>
</tr>
<tr>
<td></td>
<td>Alkaline and Peralkaline Granitoids</td>
<td>A</td>
<td>ASI = 1</td>
<td>MgO = 0.5%</td>
<td>Anorogenic Granitoids</td>
</tr>
</tbody>
</table>

Thomas 1980). As a consequence, Fe and Ti increase relative to Mg in the evolved magmas. For example, in the alkaline suites of Mount Kenya (East African Rift), the MgO/TiO₂ ratio is mainly controlled by the Ti-magnetite, then in the intermediate magmas (Price et al. 1985) it is lower (near 1) than in the calc-alkaline and tholeiitic suites of the Japan.

Similar variations of the MgO/TiO₂ ratio in relation with variable P_water conditions are also observed in orogenic and anorogenic plutonic series. Whole series, the TiO₂ and the MgO contents decrease together and the MgO/TiO₂ ratio becomes constant for MgO=2%. From this differentiation stage, the biotite and the Fe-Ti oxides are stable at the liquidus. In the anorogenic suites, Ti and Mg are concentrated in biotite and ilmenite whereas Ti enters into the spheene and the amphibole in the orogenic series.

**ASI, MgO/TiO₂, and Geodynamic Environments**

Except in the S-type suite of Chappell & White (1992), the ASI increases with the differentiation index, i.e. the decrease of MgO (in this paper). This evolution is initially quick (Fig. 1B) and becomes slow from ASI=1 on (biotite crystallization). The exception of the S-type Lachlan Belt granites (Australia) may be related to the crystallization of Al-rich cordierite, which lowers the ASI of the residual liquid, whereas in the other series the amphibole fractionation (Al-poor) increases the ASI.

Different magmatic suites reach Al-saturation (ASI=1) under MgO values specific to each one: 0.7% in anorogenic granites, 1.9% in calc-alkaline suites and 3.2% in the Al-K-series of the Vosges Mountains in France (Saleminck & Verkarrean 1989). It is noticeable that the Mg poorest suites (Corsican granodioritic series) are just Al-saturated whereas the Mg-richest suites (La Margeride, France) are characterized in biotite and ilmenite whereas Ti enters into the spheene and the amphibole in the orogenic series.

The MgO/TiO₂ ratio nears 1 in the intermediate stages of the A-type series, and 0.5 in the alkaline and peralkaline series (Fig. 2A). This feature may be related to the MgO/TiO₂-P_water relationship as the A-type anorogenic series are formed under higher P_water than the anorogenic alkaline and peralkaline series associated with the continental rifts. However, P_water is much higher in the orogenic series. Considering a restite model, the MgO/TiO₂ ratio depends on the initial magma which may be evidenced by the MgO/TiO₂ value nearing 3 (Fig. 2B) in the crustal granites (S-type of Australia and France) as well as in the earth’s crust (Taylor & McLennan 1985). In such rocks, the garnet and the cordierite, which usually occur, play an important role in the Mg partition; furthermore, the biotite is always Fe-richer than the cordierite.

The K-Al-Mg-series from Margeride (France) (Fig. 2C) is characterized by a very high MgO/TiO₂ value (~4). This series is a mixing of crustal and of lamprophyric mantle magmas (Sabatier 1984) in which the early crystallization of the biotite is a result of relatively high P_water. In such series, the MgO/TiO₂ ratio is initially fixed by the lamprophyric magma, subsequently controlled by the biotite fractionation, even if a late cordierite appears in a few massifs as in La Margeride.

In a few cases the general MgO/TiO₂-P_water relationships may be invalidated. For example in the Ibituruna syenite massif in Brazil (Bílal et al. 1991), the MgO/TiO₂ ratio is higher than 1 despite the low value (near 0.5) which would result of the alkalinity of the series. This anomaly may be due to unusual high P_water in conjuction with the shearing dynamics of the intruded crust.

The K-type granitoids of Sibiti and Margeride massifs can be grouped together on account of close similarity. Thus, chronology of tectonic can be suggested. As expressed in the Figs.1B, 1C, 2B and 2C, the chronological evolution of the ASI/MgO and MgO/TiO₂ shows three stages: (1) subduction magmatic processes (ASI=1 for MgO=1.8 and MgO/TiO₂ =2); (2) collision magmatic processes (ASI=1 and MgO/TiO₂ =3); (3) tectonic magmatism with high K-granites formation (ASI=1 for MgO=3.7 and MgO/TiO₂ =4).

Our study emphasizes the role of ASI and of MgO/TiO₂ ratio the relationship of geochemical geodynamical typologies. Both parameters may help the magmatic characterization based on major element analyses. As described in the examples cited above, such a series characterization needs to establish firstly the MgO content of rocks reacting the aluminum saturation (ASI=1) but for S-type series which are peraluminous, and secondly the MgO/TiO₂ ratio. A summary of our results is given in the Table 2. Both parameters are controlled by P_water which mainly controls the series. However, caution is necessary in one hand because the ASI is related to the alkaline elements (Na and K) which move during alteration, and in another hand because precision in low values of TiO₂ (<0.2%) needs ICP analysis rather than XRF ones.


