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# The incompatible behaviour of gold in reduced magmas: a working hypothesis

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*Key-words:* Gold; oxygen fugacity; reduced/oxidized; magnetite/ilmenite series.

*Abstract:* Gold seems to show contrasting behaviours during magmatic evolution according to the $fO_2$ of the melts. In more oxidized conditions, characterized by the presence of magnetite as the main Fe-Ti oxide, gold content in plutonic rocks decreases with increasing differentiation. On the other hand, in more reduced conditions, characterized by the predominance of ilmenite, gold content in plutonic rocks increases with increasing differentiation.

The mineral structures of the intervening minerals (magnetite and ilmenite) are compared with the possible different gold ions (aurous, $Au^{+}$; and auric, $Au^{3+}$). It is hypothesized that under more oxidizing conditions auric gold is present, which is easily incorporated in the crystallizing magnetite due to its similar size to ferrous and, to a lesser degree, ferric iron; magnetite effectively acting as a sink for the gold and causing its early removal from the melt. Under more reducing conditions, aurous gold is the only gold cation present and its larger size prevents it from being incorporated into the ilmenite (and possibly magnetite). Therefore gold behaves as an incompatible element and tends to concentrate into the late fluids, possibly leading to gold mineralization related to highly evolved fluids.

*Palavras-chave:* ouro; fugacidade do oxigénio; reduzido/oxidado; séries da ilmenite e da magnetite.

*Resumo:* O ouro apresenta comportamento distinto ao longo da evolução magmática, de acordo com a $fO_2$ do magma. Em condições oxidantes, caracterizadas pela presença de magnetite como a principal fase de óxido de Fe-Ti, a concentração de ouro em rochas plutónicas diminui com a diferenciação. No entanto, em condições redutoras, caracterizadas pela predominância de ilmenite, a concentração de ouro em rochas plutónicas aumenta com a diferenciação.

Neste trabalho, comparam-se as estruturas das fases de óxido de Fe-Ti (magnetite e ilmenite) com os possíveis iões de ouro (auroso, $Au^{+}$; e aurico, $Au^{3+}$). É formulada a hipótese de sob condições mais oxidantes ocorrer ouro aurico que, devido a ter um raio iónico similar ao ferro ferroso e, até certo ponto, férrico, é facilmente incorporado na magnetite que vai cristalizando, pelo que a magnetite actua como um sumidouro para o ouro e leva à sua progressiva remoção do magma. Sob condições mais redutoras, o único ião de ouro presente é o auroso que, devido ao seu grande raio iónico, não é passível de ser incorporado na ilmenite (nem possivelmente na magnetite). Deste modo, o ouro comporta-se como um elemento incompatível e tende a acumular-se em fluidos tardios, ficando disponível para levar à formação de mineralizações auríferas.

## INTRODUCTION

In order to help understand granite magmatism and metallogeny, Ishihara (1977; 1981) developed the magnetite-series and ilmenite-series classification scheme, based on the $fO_2$ of the melts and summarized in Table 1. According to this scheme the magnetite-series granitoids would have been derived from more oxidized magmas and are recognizable by the presence of significant amounts (>0.1 vol. %) of magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$). The ilmenite-series granitoids, on the other hand, would have been derived from more reduced magmas and have much less opaque minerals (<0.1 vol. %), ilmenite ($Fe^{2+}Ti^{4+}O_3$)

**TABLE 1**

Ishihara's classification scheme

| | **Ilmenite-series:** | **Magnetite-series:** |
|---|---|---|
| $fO_2$ of the melts: | Reduced | Oxidized |
| Opaque mineralogy: | Ilmenite >> Magnetite | Magnetite >> Ilmenite |
| Primary $Fe_2O_3/FeO$ of granitoids: | < 0.5 | > 0.5 |
| Control on $fO_2$: | Incorporation of crustal carbon | Dissociation of water |

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being the dominant one. The primary ratio $Fe_2O_3/FeO$ can be used as a parameter to distinguish the two series, if it is higher than 0.5 a rock can be classified as belonging to the magnetite series while if it is lower than 0.5 it can be classified as belonging to the ilmenite-series. Due to the different opaque mineralogy, plutons can also be classified based on their magnetic susceptibility.

According to ISHIHARA (1981) these two distinct granitoid series have substantially different origins and modes of emplacement and thereby their distribution in time and space is quite distinct. Magnetite-series plutons are generally originated at greater depths than ilmenite-series plutons. Additionally, magnetite-series plutons broadly correlate with I-type granites (igneous source rock) while ilmenite-series plutons broadly correlate with S-type granites (sedimentary source rock). Their distinct oxygen fugacity is related to the dissociation of water that acts as an oxidizing agent for magnetite series magmas or to the incorporation of crustal carbon that acts as a reducing agent for the ilmenite-series magmas. To prove the occurrence of carbon incorporation, ISHIHARA & TERASHIMA (1989) have analyzed granitoids for non-carbonate carbon, hereby showing that carbon content is appreciably higher in the ilmenite-series than in the magnetite-series granitoids.

## METALLOGENETIC IMPLICATIONS OF $fO_2$ OF MAGMAS

From the metallogenetic point of view, ISHIHARA *et al.* (1985) have shown that $fO_2$ significantly affects the gold content of granitoid rocks. In their study, based on granitoid plutons from Japan, they concluded that the average gold content of the magnetite-series rocks (4.3ppm) is almost double that of rocks of the ilmenite-series (2.5ppm). This may be interpreted as being the result of compatible behavior of gold in magnetite-series magmas, in contrast to a possible incompatible behavior of gold in ilmenite-series magmas.

As an obvious result of this interpretation, several authors have noticed the tendency of plutonic-related gold mineralization to be related to more reduced magmatic plutons, belonging to the ilmenite-series. LEVEILLE *et al.* (1988) and later MCCOY *et al.* (1997) have shown this empirical relationship by plotting composition data for both gold associated and gold devoid plutons from Alaska, Idaho and Montana (Fig. 1).

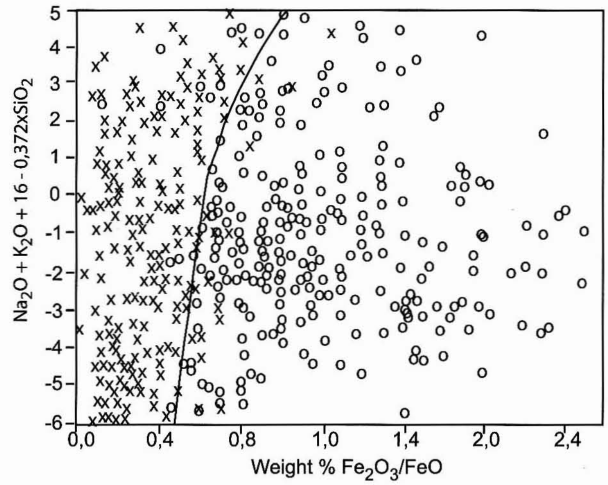


Fig. 1 – $Fe_2O_3/FeO$ ratio vs. alkalinity index plot, showing that gold associated plutons (crosses) are more reduced ($Fe_2O_3/FeO$ <0.5) than gold devoid plutons (circles). Data from North American plutons, modified after MCCOY *et al.* (1997).

Work by MCCOY *et al.* (1997) on North American plutons, has shown that the association of plutonic related gold mineralization with ilmenite-series plutons is due to the incompatible behavior of gold in ilmenite-series magmas. These authors have compared the gold content along the differentiation trend for gold favorable plutons (where gold mineralization is known to be present) and for gold devoid plutons (where gold mineralization is absent). The contrasting trends are shown in Fig. 2. Gold correlates positively with silica in ilmenite-series plutons and correlates negatively with silica in magnetite-series plutons.

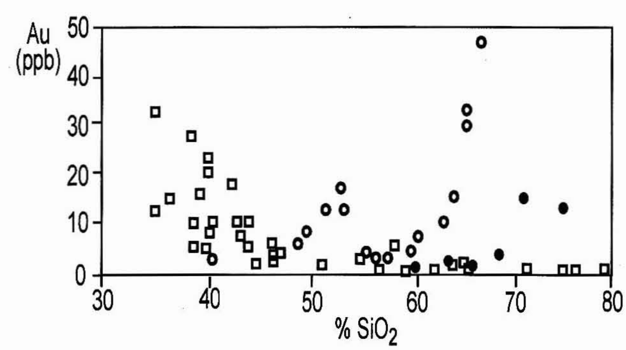


Fig. 2 – Variations in gold content with fractionation for Alaskan plutons. The ilmenite-series plutons hosting gold districts are portrayed by circles (Flat pluton represented by filled circles and Fairbanks pluton by open circles). A barren magnetite-series pluton (squares representing the Jurassic Chugach pluton) is shown for comparison. Modified after MCCOY *et al.* (1997).

The enrichment in gold along differentiation trend for the studied ilmenite-series plutons is in contrast with what was generally thought to happen during magmatic evolution (TILLING *et al*, 1973). However, KOROBEYNIKOV (1980) has already referred the tendency for gold accumulation in accessory minerals of late differentiates of some plutons, suggesting that it could behave incompatibly and concentrate in residual melts and fluids.

## WORKING HYPOTHESIS

Although the gold content from the magma source rock might significantly affect the gold content of the magma and ultimately control the presence of mineralization, it is obvious that the magma evolution process will play an even more important role. In this paper, only the magma evolution process is addressed and it is assumed that some gold is present in the magma since the beginning, which does not necessarily have to be always exact.

It is assumed that the evolution of the magmas related to the intrusion-related Au deposits described is essentially controlled by fractional crystallization. In this case, the empirical observations described above are certainly due to the fact that reduced magma (ilmenite-series) inhibits the incorporation of gold into crystallizing phases and resulting plutonic rocks. This will promote gold concentration in the latter stages of differentiation and ultimately allowing the highly evolved fluids to act as mineralizing hydrothermal fluids.

The reason for this contrasting behaviour must be associated with the structure of the minerals that form in the two different magma series, their available cation sites and/or with the dominant gold species present under different fO2 conditions. The radii of the cations involved are shown in Table 2.

**TABLE 2**

Cation radii

| Cation: | $Fe^{2+}$(ferrous) | $Fe^{3+}$(ferric) | $Au^{+}$(aurous) | $Au^{3+}$(auric) |
|---|---|---|---|---|
| Radii (Å): | 0.92 | 0.785 | 1.46-1.49 | 0.910 |

## DATA FROM SHANNON & PREWITT (1969)

From the analysis of the cation radii, the factor that most affects their distribution into mineral phases, it is apparent that $Au^{3+}$ is very similar to $Fe^{2+}$ and therefore might substitute for it. Applying Paulings' 1st rule:

$$\left.\begin{array}{ll} Au^{3+} & R_{cation}/R_{anion} = 0.910/1.26=0.722 \\ Fe^{2+} & R_{cation}/R_{anion} = 0.92/1.26=0.730 \end{array}\right\} \text{6-fold coordination}$$

$$Au^{+} \quad R_{cation}/R_{anion} = 1.46/1.26=1.159 \qquad \text{12-fold coordination}$$

It is evident, from the above, that $Au^{3+}$ can substitute for $Fe^{2+}$ in 6-fold coordination positions of the magnetite and ilmenite structures, which is not possible in the case of $Au^{+}$ because no 12-fold coordination positions are available in these minerals.

It might therefore be concluded that it is not the crystallizing oxide mineral that controls the incompatible behaviour of gold, but rather the gold species present.

Although never dominant under typical magmatic conditions, minor amounts of $Au^{3+}$ might be present under relatively oxidizing conditions, characteristic of magnetite-series magmas (ROMBERGER, pers. comm.) Therefore, it is proposed that in magnetite-series magmas, this available $Au^{3+}$ will readily fit into the $Fe^{2+}$ site of magnetite, or eventually into the $Fe^{3+}$ site if a coupled substitution is to be avoided. It is for this reason that magnetite of granitoid rocks has been reported to contain up to 1ppm Au (LEVEILLE *et al*, 1988). Supporting this, work by MIRONOV & ZHMODIK (1980) using gold radioisotopes established that gold enters the lattice of magnetite, as well as the lattice of some sulfides. Furthermore, as $Au^{3+}$ gets incorporated into the crystallizing magnetite it promotes the oxidation of $Au^{+}$ to $Au^{3+}$ so that, if this happens for a long enough period of time, all the gold will end up in magnetite. This model assumes that species equilibration is more rapid than mineral growth and diffusion. In this way, gold will not be available to concentrate in residual fluids that could lead to mineralization.

On the other hand, under more reduced conditions (characteristic of ilmenite-series magmas), the only gold ion present will be $Au^{+}$, with its large size preventing its incorporation into any of the oxide minerals or possibly sulfides. The preference of gold for establishing covalent bondings will also prevent it from being incorporated into ionic cation sites, even if their size is adequate, as would be the case for replacing $K^{+}$ in biotite or K--feldspar. This will promote the concentration of gold into highly evolved magmatic fluids, ultimately leading to mineralization.

As proposed, gold speciation is intimately related to the oxidation state of the magma, whereby $fO_2$ effectively controls the behaviour of gold. NECRASOV (1996) compared the speciation of gold with the activity ratios of $Fe^{3+}$ and $Fe^{2+}$. This author refers to a work by LETNIKOV & VILOR (1981) that demonstrated that the increment of the activity of $Fe^{2+}$ (reduction) tends to stabilize $Au^{+}$ while the increment in the activity of $Fe^{3+}$ (oxidation) will promote the stabilization of $Au^{3+}$.

## COMPARISON WITH OXIDATION STATE RELATIONSHIPS IN BASIC MAGMAS (CARMICHAEL & GHIORSO, 1986)

As CARMICHAEL & GHIORSO (1986) have noticed, melts tend to evolve along paths with constant $Fe_2O_3/FeO$ as fractionation proceeds. Since $Fe^{2+}$, rather than $Fe^{3+}$, tends to be used up early (in olivine and pyroxenes) one would expect that the melt's oxidation state would increase. The authors' explanation for this considers that the iron redox system is coupled with the sulfur redox system that will act as a self-regulating internal oxygen reservoir, thereby constraining the evolving melt to a constant $Fe_2O_3/FeO$ by means of the reaction:

$$SO_4^{2-} + 8FeO = 4Fe_2O_3 + S^{2-}$$

Gold may be involved in a similar coupling of redox systems allowing the gold in the melt to oxidize as auric gold is being incorporated into crystallizing phases.

## REMARKS

As a concluding remark it should be referred that HEDENQUIST & LOWENSTERN (1994) consider that pyrrhotite constitutes a common phenocryst host for gold in granites. This is supported by the radioisotope work by MIRONOV & ZHMODIK (1980), described earlier.

Therefore, it should be pointed out that for gold to behave as an incompatible element, besides the relatively reduced nature of the magma, it might be important that its sulfur content is low enough so that no sulfides crystallize, since sulfides (namely pyrrhotite and chalcopyrite) act as sinks for gold, even more effectively than magnetite.

## CONCLUSIONS AND EXPLORATION IMPLICATIONS

The empirical data presented indicates that gold behaves incompatibly only if magmas are sufficiently reduced (ilmenite-series magmas). This is caused by the large size of the only gold cation present under these conditions ($Au^{+}$) that prevents it from being incorporated into the crystallizing oxides and, possibly, sulfides.

This has major implications in the exploration of plutonic-related gold deposits since the metallogenetic model for this type of deposits implies that gold has to behave incompatibly, thereby excluding magnetite-series plutons as adequate targets. Exploration efforts should therefore be focused on ilmenite-series plutons.

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