

RUTILE CRYSTAL CHEMISTRY FROM THE EL TENIENTE PORPHYRY COPPER DEPOSIT, CHILE

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KEY WORDS: Rutile, trace elements, mineralization indicator, Andean porphyry copper deposits, El Teniente.

INTRODUCTION

In sub-volcanic porphyry intrusives and their enclosing rocks, rutile is the dominant Ti-bearing phase. The hydrothermal alteration of pre-existing Ti-bearing minerals such as ilmenite, Ti-magnetite, sphene, hornblende or biotite, leave behind "residual" TiO₂, as rutile (and perhaps anatase). This process, first recorded in porphyry copper deposits by Williams and Cesbron (1977), is best developed in the potassic alteration zone, where rutile is virtually the only Ti-bearing accessory phase and occurs contemporaneously with the sulfides. It is also very common in phyllic alteration zone (Williams and Cesbron, 1977; Garnar and Stanaway, 1994; Evans, 1994).

Apparently, ilmenite formation in these environments is prevented by the removal of Fe into newly forming sulfides, while sphene and perovskite fail to form because the aqueous fluids remove Ca to the outer, lower temperature alteration zones.

Rutile starts crystallizing at the beginning of the deuteric stage in the porphyry intrusion, and continues forming outward in the wallrocks from it during the metasomatic and hydrothermal stages (Williams and Cesbron, 1977).

The fact that rutile derived from the alteration process of primary Ti-bearing minerals is related to Cu-mineralizing fluids, and that the rutile structure can allocate a broad spectrum of different cations (Waychunas, 1991), makes this Ti-oxide a potential "monitor" of the chemistry of the hydrothermal fluids and mineral reactions occurring in such mineralizing processes.

In spite of the local presence in porphyry systems of anatase filling veins, suggesting that on a local scale, titanium can be mobile (Rabbia, et al 1998), the general insolubility of rutile in near surface conditions makes, Ti very immobile during weathering and low grade metamorphism (Pearce and Cann, 1973).

The strong covalent nature of Ti-O chemical bonds, confers to rutile a high physical stability. This robustness, coupled with the capacity to allocate a great variety of trace elements, allows it to be considered as a resistate mineral with a potential to be used as a "pathfinder" in exploration.

With respect to Andean porphyry copper deposits, there is a particular lack of information on the characteristic trace element content of rutiles in these environments. This information is necessary in order to use this Ti-oxide as a mineralization indicator.

The preliminary chemical results reported here are part of a systematic study on the crystal chemistry characterization of rutiles from Andean porphyry copper deposits, and includes the El Teniente, Chuquicamata and El Salvador deposits.

RESULTS

Samples from the El Teniente porphyry copper deposit include both the dacite porphyry and the host andesite (mine rock classification). Superficial (2380 m.a.s.l.) and deep (1473 m.a.s.l.) parts of the mineralized column, as well as both hypogene and supergene mineralization were also sampled.

Microprobe analyses indicate the presence of the following elements in the structure of rutile from both rocks types: Ca^{+2} , Fe^{+3} , Cr^{+3} , Sc^{+3} , Al^{+3} , V^{+3} , Si^{+4} , Sn^{+4} , Zr^{+4} , Nb^{+5} , Ta^{+5} and W^{+6} .

The total trace elements content of rutiles in dacites, range from 1.0 to 10.1 wt%, with a mean content of 2.8 wt% (n=139). To andesites, it ranges from 1.0 to 14.1 wt%, with a mean content of 3.1 wt% (n=130). Maximum registered values (table 1) and mean values (table 2) of individual oxides in rutiles from the two rock types are:

Table 1

Oxide wt%	SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	V_2O_3	Sc_2O_3	SnO_2	Nb_2O_5	Ta_2O_5	WO_3
Dacite	1.03	1.26	4.36	0.21	1.26	0.56	0.07	0.53	0.23	5.62
Andesite	4.41	1.39	6.61	0.78	0.54	0.05	0.17	0.61	0.28	8.66

Table 2

Oxide wt%	SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	V_2O_3	Sc_2O_3	SnO_2	Nb_2O_5	Ta_2O_5	WO_3
Dacite	0.060	0.056	1.188	0.040	0.336	0.021	0.014	0.132	0.038	0.873
Andesite	0.173	0.074	1.392	0.085	0.194	0.006	0.020	0.060	0.029	1.076

Figure 1 ($\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$) illustrates for the dacite porphyry a tendency to increase the $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ ratio in rutiles with depth. This tendency is also noted in rutiles coming from andesites (not shown here).

The total trace element content of rutile (not shown here) from either the dacites or andesites, do not shows any clear pattern with respect to the depth. Notwithstanding, the maximum values tend to occur in the deepest samples.

DISCUSSION AND CONCLUSIONS

With respect to the total trace element content in rutile, it can be assumed that for similar environments of precipitation, the higher the temperature of formation, the higher the expected trace element content. Consequently, in the deposit an increase in total content is expected with depth. With the exception of high trace element contents in the deepest analyzed samples, the data do not show any clear pattern of variation, suggesting that local high fluid/rock interactions modified the expected general trend.

The broad spectrum of cations found in El Teniente rutiles is identical to that identified at Cerro Pelado, a rhyolitic satellite prospect next to the El Salvador mine (Rabbia et al. 1998). The different lithologies (andesite-dacite to rhyolite) do not appear to exert an important control on the type of element present in the rutiles, suggesting that the fluid composition plays an important role, and thus pointing to a distal source for the elements present in rutile. However, important differences in concentration and elemental ratios appear when the different host rocks are considered (see table 1 and 2), indicating that the bulk rock composition effect cannot be ruled out.

Oxides ratios were used in order to minimize the effect of different fluid/rock ratios. The $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ ratio increases systematically with depth (see fig.1), suggesting a possible combination of temperature and $f\text{O}_2$ dependence. The $f\text{O}_2$ conditions appears to be particularly important for V enrichment in rutiles from the oxidized superficial parts of the deposit in which supergene enrichment processes take place. Part of the V in these rutiles, must be V^{+4} , since V changes to valency 4+ when $f\text{O}_2$ is close to that defined by the magnetite-hematite equilibrium and proxies mostly for Ti^{+4} in rutile (Schuiling and Feenstra, 1980).

The elements present in the rutile structure must be carefully evaluated before attempting any interpretation of its origin. Based on the distance to the source, two different scenarios for the origin of these elements can be envisaged, a local and a distal one.

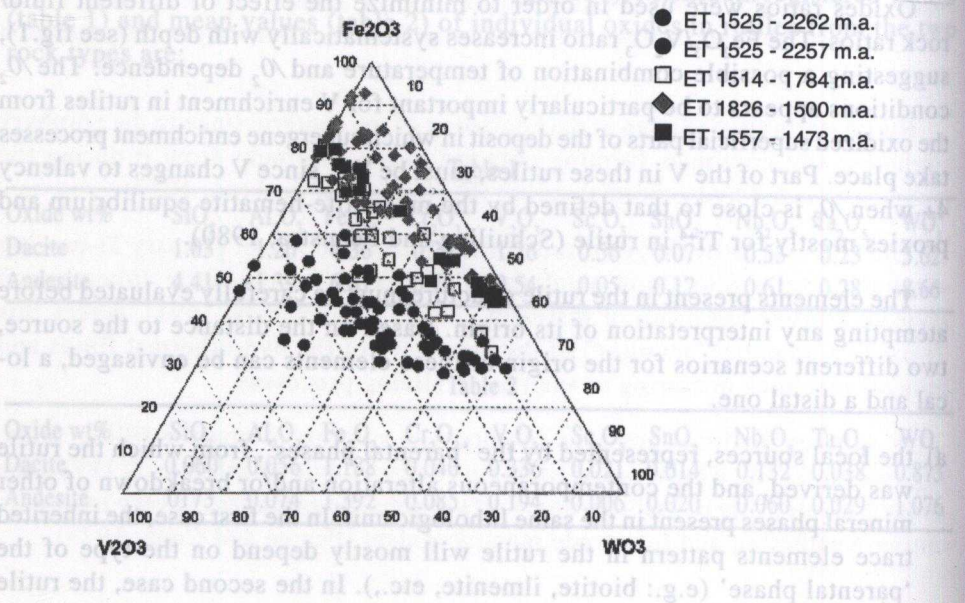
- a) the local sources, represented by the 'parental phases', from which the rutile was derived, and the contemporaneous alteration and/or breakdown of other mineral phases present in the same lithologic unit. In the first case, the inherited trace elements pattern in the rutile will mostly depend on the type of the 'parental phase' (e.g.: biotite, ilmenite, etc.). In the second case, the rutile

chemistry is basically constrained by the host rock chemical composition ('bulk rock composition effect'). Both yield additional information pertaining to the local redistribution of elements released during the hydrothermal alteration processes.

b) the other potential scenario is represented by a distal source, in which lithologic units, other than those hosting the analyzed rutile, can be scavenged by the circulating fluids thus becoming the source for elements that finally become incorporated in the rutile structure. Furthermore, the magmatic center itself may represent another distal source of components that can also be allocated in rutile.

At present, discrimination between local and distal sources is precluded by the absence of a complete trace elements characterization of rutile and rutile's parental phases, coupled with the complete lack of rutile/fluid partition coefficients ($Kd^{rutile/fluid}$) under conditions representative of Andean porphyry copper deposits. Ongoing work is underway in order to address this information gap.

Figure 1. (Fe_2O_3 - V_2O_5 - WO_3) ternary diagram showing the tendency of increasing Fe_2O_3/V_2O_5 ratio in rutiles from dacite porphyry with depth. Solid diamonds and squares are the deepest samples (1473 and 1500 m.a.s.l.), solid dots are the more superficial samples (2257 and 2262 m.a.s.l.) and have supergene enrichment processes over superimposed.



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This abstract is a contribution to the FONDECYT Project #1980511

'Evaluation of rutile as a metal content monitor of hydrothermal fluids associated with Andean porphyry copper deposits: crystal chemistry study and base metal $K_d^{Rutile/Fluid}$ experimental determination.

SAMPLES AND ANALYTICAL METHODS

Emeralds used in this study were collected from 62 occurrences and deposits in 19 countries. The extraction of framework oxygen from emerald was done using standard techniques with BrF_3 as the reagent (Clayton and Mayeda, 1963). The oxygen released from 5 to 10 mg of emerald was converted to CO_2 in a graphite furnace at 750°C and the yields measured by a capacitance manometer. All the analyses were duplicated (sometimes triplicated) and standards (international quartz NBS 28, $\delta^{18}\text{O} = +9.6\%$ or laboratory : quartz NL 615, $\delta^{18}\text{O} = +18.3\%$) were measured for each experimental run. The $^{18}\text{O}/^{16}\text{O}$ ratio of CO_2 was analyzed on a gas-source spectrometer (VG 602D). The $\delta^{18}\text{O}$ -values are presented in the

chemistry is basically constrained by the host rock chemistry (both 'matrix' and 'inclusion' effects). Both yield additional information on the processes.

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incorporated in the rutile structure. Furthermore, the magmatic rutile may represent another source of vanadium in the rutile. (1971) using trace element analyses. Earth Planet. Sci. 19, pag. 290-300.

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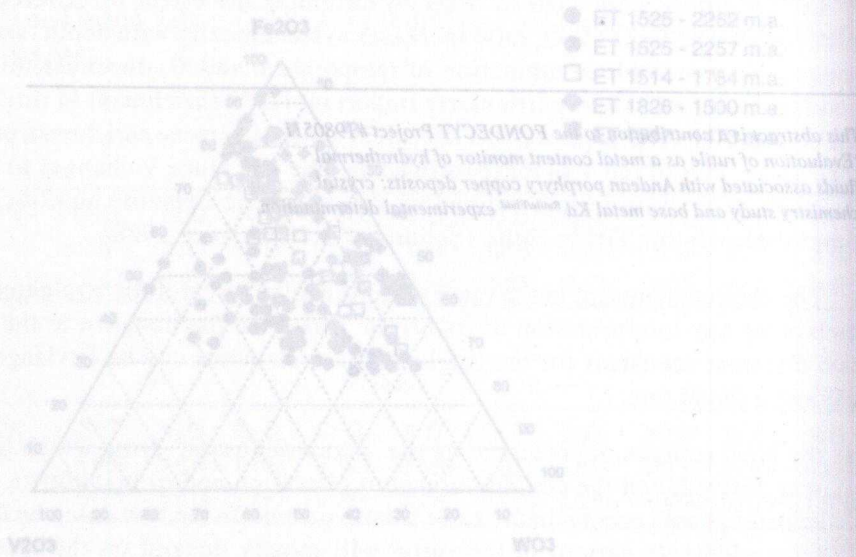


Fig. 1. Ternary diagram showing the dependence of rutile composition on the metal content of the host rock. The diagram is based on the data of Williams et al. (1977) and is plotted in terms of Fe₂O₃, WO₃ and TiO₂. The legend indicates the different samples used in the study.