

# The chemical composition and paramagnetism of auriferous quartz

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## Introduction

A visiting geochemist from South Africa pointed out to me in 1983 on an excursion to Norseman in Western Australia that gold bearing quartz exhibits frequently a bluish colour like blubber, in contrast to the white colour of barren quartz. This visible property makes it vaguely possible in a specific mine area to assess with the naked eye whether quartz will contain gold (at ppm level) or not. Fascinated by this piece of information I spent the following two years in the Central Science Laboratory of the University of Tasmania assessing series of microcrystalline quartz samples from gold mines in Tasmania (mainly Beaconsfield), Victoria (Bendigo and Stawell), New Zealand (Waihi and Karangahake), Spain (Rodalquilar) and also all the specific quartz samples with visible gold from the collection of the Museum of Victoria in Melbourne.

## Instrumentation

All methods used were physical: thermoluminescence, cathodoluminescence, Raman, infrared and electron paramagnetic resonance spectroscopy, of which the last method proved to be the most suitable. The outcome of the simple powder EPR spectroscopy at room temperature was that barren quartz shows invariably flat EPR spectra and that auriferous quartz may or may not show a strong EPR centre, which represents what may be loosely defined as the Al-O centre, the replacement of Si in the SiO<sub>2</sub> lattice by Al. This substitution causes the quartz to be weakly paramagnetic, too weak to be picked up by a conventional Gouy balance, but strong enough to cause electron paramagnetic resonance if the sample is placed in a microwave of constant frequency at specific flux densities of a changing strong external magnetic field. 'X-band' EPR powder spectroscopy of quartz was then tested as an exploration tool for a period of about three years, in spite of difficulties with the interpretation of the spectra and the sometimes ambiguous results.

Because of suspected presence of ions compensating for the charge imbalance caused by the Al in

the quartz lattice, chemical analyses were performed by conventional and also Zeeman atomic absorption spectroscopy. These analyses suggested a positive correlation between K, Na and sometimes Li, Al and the EPR signal, and indirectly with the presence of gold. The atomic absorption techniques involved sample digestions causing loss of some elements and were poorly suited to the low concentrations of Al in quartz. Difficulties were also encountered with XRF spectrometry, insensitive for low level of Al and Na and unable to detect Li.

From 1989 proton induced X-ray emission spectroscopy at the Australian Nuclear Science and Technology Organisation Laboratories, later combined with proton induced gamma ray emission spectroscopy for the light elements Li through to Al, solved these analytical problems. Combined PIXE-PIGME analysis can provide a spot or bulk chemical analysis down to or below ppm level for sixty elements simultaneously (Bird, 1989; Cohen and Clayton, 1989).

## Results

The outcome of several hundreds of analyses is that in general auriferous quartz is relatively rich in trace elements, usually Al and K, often F, Ti, Fe, Ge, As, Rb and sometimes Li and Na, and also Zr compared with barren samples from the same area. All these microcrystalline quartzes contain higher trace element concentrations than those reported in the literature for well shaped quartz crystals. The relations between the elements show in most cases a good correlation between the sum of the molecular proportions of K, Na and Li and the sum of the molecular proportions of Al, Fe, Ti, Mn and Zr. Variations in chemical composition however occur between goldfields and include variations in the K, Na, Li and Rb ratio. Another difference appears to be that Ge is present at the level of several ppm in mesothermal and hypothermal auriferous quartz but not appreciably in epithermal quartz. The chalcidony from Carlin is not only characterised by high K contents but also by high Rb and V values, more than in any other type of gold deposit studied (van Moort

and Hotchkis, 1993).

A further result is the good correlation between the trace elements and the intensity of the EPR signal, viz. the  $[\text{AlO}_4]^\ominus$  centre, particularly for K and Al, and also Ge if present.

The outcome of two thousand EPR analyses is that it is possible to describe complex vein systems by a taxonomy of spectral shapes and intensities. Basically the spectra are still poorly understood, although characteristic Al, Mn, Fe, Cu and Ge centres can be recognised in addition to radiation induced defects.

In most cases it is possible to predict on the basis of a combination of trace elements in the quartz samples if the sample itself and adjacent material will contain gold, (as determined by fire assay). The EPR analyses are less reliable in this respect.

### Discussion

The positive correlation between the concentrations of K, Na and Al, Fe, Ti, Mn and Zr in the quartz studied is too strong to be of purely coincidental nature. The simple relations indicate a balance between electron donors, electron acceptors and compensating ions. All areas studied show basically the same relations, with a predominance of K over Na and Li and also with more Al than previously found in quartz. These relations between the elements are particularly straightforward in material studied from Beaconsfield in northern Tasmania and Victoria. There is rarely evidence that mineral inclusions like sericite are responsible for the elemental distributions, but it remains possible that at the levels of concentration present such inclusions may have escaped detection during selection and later electron microprobe inspection of the quartz. A more likely explanation is that the elements are substitutional in the quartz lattice and are at the same time responsible for the stronger than anticipated paramagnetic resonance. The EPR spectra of the microcrystalline material are comparable to published quartz spectra, albeit usually stronger. The intensity of these quartz spectra correlates well with its K, Li, Na, Al, Rb

and Ge content. This suggests presence of Al and Ge substituting for Si in the lattice with Li and Na (and possibly K) as charge compensating ions.

Geological and petrographical evidence indicates that most of the auriferous quartz veins were rapidly formed in fracture zones (Russel and van Moort, 1992). Such rapid deposition will lead to precipitation of microcrystalline quartz rich in trace elements. The trace element concentrations content of all our material is indeed high compared with that of macrocrystalline quartz, but comparable with values for the few studies of gold bearing quartz veins available in the literature. The solubility of quartz is strongly temperature dependent and its precipitation will be caused by a drop in temperature in ascending hydrothermal fluids.  $\text{GeO}_2$  is at higher temperature much more soluble in water than  $\text{SiO}_2$ . Consequently it is an element enriched in late magmatic and hydrothermal fluids. The gold is presumably precipitated through destabilisation of gold complexes in rapidly rising fluids. Consequently, the positive but imperfect correlation of the trace elements mentioned and the intensity of the EPR signal with the presence of gold appears to be coincidental.

### References

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