



# CRYSTAL CHEMICAL FEATURES OF WATER AND IMPURITY INCORPORATION IN NATURAL QUARTZ

D.B. Gubareva<sup>1</sup>, N.G. Stenina<sup>1</sup>, A.K. Gutakovsky<sup>2</sup>

<sup>1</sup>Institute of Geology SB RAS, 630090, Novosibirsk - 90, Russia

<sup>2</sup>Institute of Physics of Semiconductors, 630090, Novosibirsk-90, Russia

Silicon dioxide is one of the most abundant compounds of the Earth's crust. It forms numerous minerals (silica varieties) differing in physical chemical properties and structure-textural features. Silica mineral forms are stable in a wide range of pressure, temperature and chemical conditions. That is why these natural compounds are of great importance both in basic and applied aspects of material sciences.

Despite the fact that SiO<sub>2</sub> has been thoroughly investigated, the principal question of the impurities and water speciation in quartz is still under discussion. Its solution is of practical significance as the formation of a specific silica variety and its properties are controlled by the mode in which water and trace elements are incorporated in the SiO<sub>2</sub> - matrix.

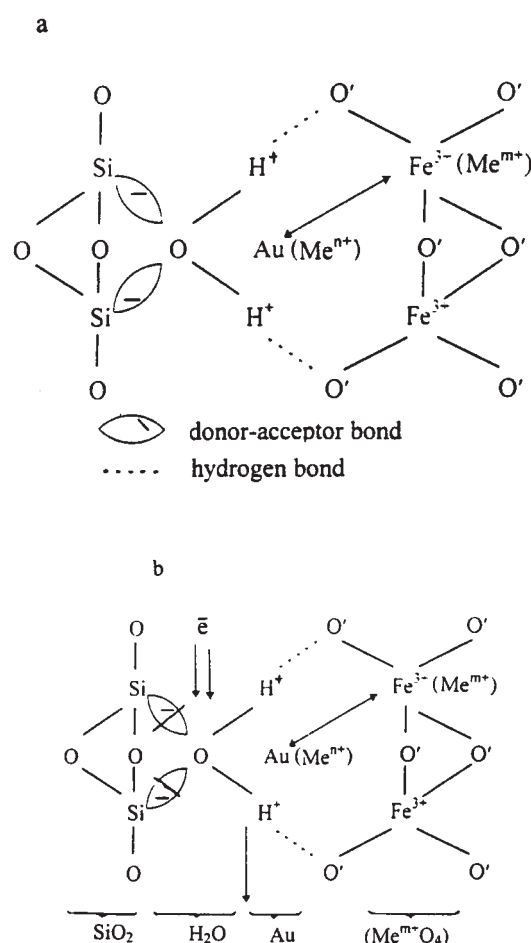
## 1. Data on water and impurity state in quartz

Infrared spectroscopy (IRS) is the principal method for the study of water speciation in minerals nominally free of water, to which quartz is also belongs [1]. There are two forms of water in SiO<sub>2</sub>: free and structural [2-4]. Free water, contained mainly in gas-fluid inclusions or adsorbed on microcracks surfaces in the sample bulk does not influence greatly crystal chemical features and properties of quartz. Therefore it is of less interest for the present researches.

Structural water causes two kinds of infrared peaks: sharp pleochroic peaks and broad (within the range of 3000 - 3600 cm<sup>-1</sup>) isotropic peak centred at 3400 - 3450 cm<sup>-1</sup>. The first are assigned to crystallographic H-defects, and the second - to gel-like H-defects [3]. In contrast to free H<sub>2</sub>O, structural water is recorded at the low temperature (77 K) IRS spectra by the wide absorption peaks mentioned above [2].

Investigations of different H- related defects in quartz by means of X-ray, TEM, AAS, EPR and other methods revealed that all of them have a complex structure and composition. However, their interpretation remains contradictory up to now. It is evident from the literature data, that water in such defects is bonded simultaneously with different cations despite its speciation: OH, H, H<sub>2</sub>O, H<sub>3</sub>O [5]. This fact explains: i) a wide range of frequencies of sharp pleochroic peaks [6]; ii) the established phenomenon of equal changes of frequencies of different sharp pleochroic peaks attributed to various H-Me defects under heating or irradiation [4]; iii) the increased contents of trace elements with different valency simultaneously dissolved in H-defects in comparison with the surrounding matrix [7, 8] At the same time, such complex defects are structurally bonded in the silicate host matrix. It is revealed by the fact,

that sharp pleochroic peaks are highly polarized and their intensities depend strongly on the sample location being investigated [3, 4]. Brunner with coauthors [3] found new lines at 894 cm<sup>-1</sup> and 916 cm<sup>-1</sup>, which they ascribed to lattice vibration of quartz, whose group of symmetry has been lowered because of incorporation of the water-related defects.



**Fig. 1.** Model of the aquacomplex. Me<sup>n+</sup> (n=1, 2) is Na, K, Li, Fe<sup>2+</sup> and other uni- or bivalent cations; Me<sup>m+</sup> (m ≥ 3) is Al, Fe, B, P and other polyvalent ions; O' - is O, F, Cl, S and other volatile elements; a- integrated state of the aquacomplex; b - disintegration into constituting parts: SiO<sub>2</sub> (left), H<sub>2</sub>O (center), Me<sup>m+</sup>O<sub>4</sub> (right).

The most adequate model, which is consistent with the data obtained earlier on H-defects, is a model of water-impurity defect in quartz (aquacomplex) [9, 10]. The aquacomplex shows how silica and metal oxide radicals are bonded via a water molecule into a single unit (Fig.1a). The central part of the aquacomplex is a tetrahedrally charged

water molecule. It forms donor-acceptor bonds with the left part ( $\text{SiO}_2$ ) and hydrogen bonds with the right part ( $\text{Me}^{m+}\text{O}'_4$ ) ( $m \geq 3$ ).  $\text{Me}^{n+}$  ( $n = 1, 2$ ) cations occupy interstitial positions between ( $\text{Me}^{m+}\text{O}'_4$ ) polyhedra.

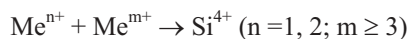
Aquacomplexes were discovered as growth defects in quartz of different genesis. Crystal chemical interpretation of the aquacomplex, presented in the Fig. 1a, was made on the basis of: i) the data of quartz examination by TEM combined with X-ray microanalysis, IRS and EPR methods; ii) the results of special experiments on quartz heat treatment; iii) analysis of literature data on the water and impurity incorporation in different silica varieties.

The aim of this study is to investigate microstructural and crystal chemical features of natural quartz of gold-bearing veins.

## 2. The problem

Natural vein quartz is extremely heterogeneous as concerns its physical and chemical characteristics. Often up to 5-7 silica varieties can be identified within a quartz-ore vein body. They vary in texture, color, transparency, density, mechanical properties and other parameters. Two contrasting quartz varieties among these forms, named hereafter QuI and QuII, were chosen for our complex examination.

QuI and QuII varieties were identified earlier as a result of investigation of a  $\text{SiO}_2$  - Cu - Mo vein system [11]. It was shown, that this quartz variability is caused by different water and metal speciation in the silica matrix. In QuI, water and metals enter the  $[\text{SiO}_4]$  - framework according to the scheme of heteroisomorphic substitution:



They are bonded in the complex  $[\text{2SiO}_3 - \text{OH}_2 - (\text{Cu}, \text{Me}^{n+})_2(\text{Mo}, \text{Me}^{m+})\text{O}'_4]$  defects (Fig.1a). These defects are incorporated in quartz structure as single defects and clusters of submicron to micron size (gel-like defects). In QuII, water is in a free form.

It is of principal interest to get a further justification for this model for the  $\text{SiO}_2$  - Au - Fe geochemical system, realized in hydrothermal veins with Au - Fe mineralization.

The concept of aquacomplex reduces the problem of water and impurity state in quartz to the one concerning mainly water speciation in its matrix. The latter, in its turn, allows combining various instrumental methods most purposefully. It is necessary that TEM methods resolving lattice defects be complemented with IRS, X-ray, thermal and chemical analyses. According, IRS was used to identify water forms in quartz; X-ray diffraction - to obtain summary characteristic of the degree of quartz lattice strain; thermogravimetry - to determine features of water bonding in contrasting quartz samples, and atomic absorption spectroscopy - to find trace elements in the quartz varieties chosen.

## 3. Experimental procedure

Our samples originate in quartz-gold-sulfide veins of the Sarala ore field, Kuznetskii Alatau (Russia). The quartz forms with the most contrasting physical and optical properties are represented by the following varieties:

QuI is gray to dark gray in color, transparent and does not contain inclusions of gas-fluid or ore phase; it is not cracked and displays a flame like morphology.

QuII is white (milky) and sugarlike, opaque; it has a lot of gas-fluid and other inclusions, and forms grained aggregates.

Single phase powder fractions of QuI and QuII were thoroughly selected from the bulk vein quartz for chemical analysis by atomic absorption spectroscopy (AAS, AS - 9 device); X-ray diffraction (URD - 63); thermogravimetry (TG, TG - 50 Mettler GA 3000, peak temperature 700 °C and heating rate 10 °C/min). Double - polished plates, where dominate either QuI, or, alternatively, QuII, were examined at room temperature and at liquid nitrogen temperature by means of infrared spectroscopy (IRS) with a Specord-75 instrument. Transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) (electron microscope JEM 4000EX) were performed on ion-thinned QuI and QuII, as on QuI, annealed at 700 °C for 100 hours.

## 4. Results

AAS has shown significant differences between the compositions of QuI and QuII, Table 1.

**Table 1.** Trace elements contents in contrasting QuI and QuII.

Quartz	Element, g/t					
	Al	Na	Li	Fe	Au	Ag
QuI gray	1820	146	0.88	1660	5.23	4.29
QuII white	1620	52	0.3	900	0.044	0.18

Au content of QuI is two orders higher than that of QuII. Among the elements analysed, it correlates best with iron.

IRS data revealed that contrasting QuI and QuII are characterized by different form of water. The high absorption of the water related peak for QuI as well for QuII indicates high water contents in both varieties (Fig.2). The low-temperature IRS spectra permit the distinction between structural and free water forms in the mineral. The H-absorption of QuI and QuII at 77 K displays the following features (Fig.2, dashed line). The broad (between 3000 and 3600 $\text{cm}^{-1}$ ) isotropic peak centred at 3450  $\text{cm}^{-1}$  practically does not change for the samples, where QuI dominates. According to Brunner with coauthors [3] and Kats [4], this peak is attributed to the molecular water in the un-ordered  $\text{SiO}_2$  environment (gel-like defects). For QuII this peak displaces completely to the ice band at 3200 $\text{cm}^{-1}$ .

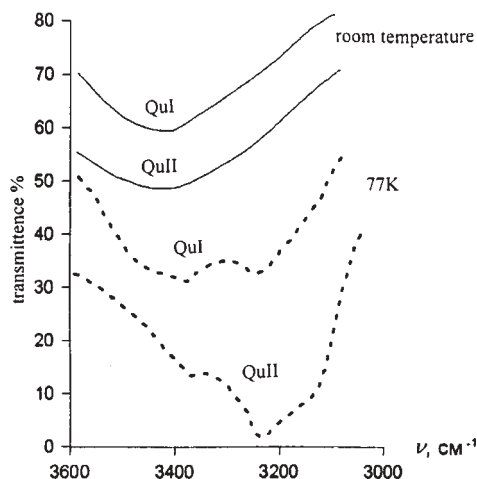


Fig. 2. IRS spectra of contrasting QuI and QuII at room and liquid nitrogen temperature

These data allowed us to conclude that structural molecular water is a characteristic species for gray QuI. Free water form is typical for the milky white QuII.

The TG curves (Fig.3) show a principally different mode of water escape from QuI and QuII during heating at 700 °C. Molecular water of the QuI escapes at 650°C, and the only narrow peak of the sample weight loss means that water is crystallographically bonded in the host silica matrix (Fig.3, line 1). Judging from temperature of the water loss, H<sub>2</sub>O is bonded with the local surrounding in QuI much strongly than water species in QuII. Total water content in QuI is higher by a factor of 2,5 compared to QuII. The latter has two diffuse peaks with maxima at 300 °C and 450 °C (Fig.3, line 2). This indicates that there is a wide range of chemical bonds with different lengths between water and silica matrix, and all of them are weaker than that in QuI. At the same time, these water forms are not definitely fixed in the matrix. The data allow us to conclude that water is crystallographically tightly bonded in the SiO<sub>2</sub> framework of QuI. As for QuII, its water gives a wide range of species: from free to weakly bonded structural forms.

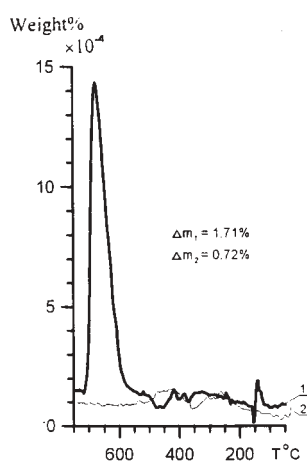


Fig. 3. TG curves of water escape from QuI (line 1) and from QuII (line 2)

X-ray diffraction shows, that QuI is characterized by diffuse peaks as it is shown on the fragment of diffraction pattern with hkl: 212, 203, 201 (Fig.4, line 1). In contrast, QuII displays sharp, well resolved peaks with a distinct  $\alpha_1$ - $\alpha_2$  splitting (Fig. 4, line 2). Assuming that the conditions of X-ray diffraction are the same for both samples, the perfection of their lattices can be compared qualitatively. For this purpose values of  $\langle \varepsilon^2 \rangle$  were calculated as  $1.75 \times 10^{-2}$  and  $1.36 \times 10^{-2}$  for QuI and QuII respectively. It is evident that the QuI lattice is more strained and consequently more defective than the QuII lattice. After annealing QuI at 700 °C for 100 h (to a temperature slightly above the temperature of the structural water escape) its peaks profile and value of  $\langle \varepsilon^2 \rangle$  ( $1.37 \times 10^{-2}$ ) become quite similar to that obtained for initial QuII. In other words, strained and defective QuI lattice is refined of existing defects and becomes more perfect.

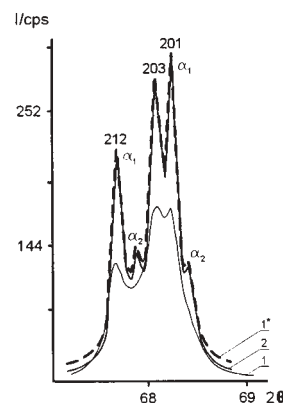


Fig. 4. Fragments of the powder patterns: line 1- QuI, line 2 - QuII, line 1\* - QuI, annealed at 700 °C, 10 h

TEM shows that microstructural features of QuI and QuII are principally different (Fig. 5). QuI has a single-crystalline structure with growth dislocations (density  $10^8 \text{ cm}^{-2}$ ). Electron microscopic images of the QuI microstructure quickly change under electron irradiation (Fig. 5a). At first, new defects with black dots diffraction contrast appear, further micropores become detectable. It allows us to conclude that initially QuI contains solid impurities and water dissolved in the matrix. Under electron irradiation, they escape from the silica framework and precipitate in a free form. The last stage of this process leads to the amorphization of the studied quartz cut. This phenomenon has been known for natural quartz [12, 13]. Amorphization occurs as a result of disintegration of complex silica-water-metal oxide defects fitted into the quartz framework. The reason of this process is illustrated in Fig. 1b. Inelastically scattered electrons during electron irradiation are captured by unsaturated donor-acceptor bonds in the left part of the complex defect. As the result, SiO<sub>3</sub>-OH bonds break up, water and interstitial impurities escape from the SiO<sub>2</sub> matrix [10]. Similar alteration of quartz occurs during its heating up to 700 °C.

QuII has mosaic substructure with a block dimensions from one to several microns (Fig. 5b). This quartz displays

rather perfect microstructure within the single blocks and high dislocation density in the low angle interblock boundaries. Gas-liquid filled micropores of submicron sizes were observed in the most large blocks. These features point that QuII has been formed as a result of recrystallization.

HREM was used to resolve solid precipitation after heating. Fig.6 illustrates crystalline cluster of 46 Å size in the SiO<sub>2</sub> amorphous matrix. Features like these were not observed in the QuI samples before their heat treatment. In the particle of the equilateral triangle form there are resolved 17 atomic planes with an interplanar distance of 3.5 + 0.02 Å (the error of measurement is determined by calibration procedure). The crystal habit points to the (111) isolation of (*Fm3m*) cubic phase in the SiO<sub>2</sub> matrix. Among the trace elements detected in QuI (Table 1) gold is the most proper candidate to make such cluster. This is supported by: i) the interplanar spacing of 2.35 Å corresponds to  $d_{111}$  of gold (*Fm3m*); ii) equilateral triangle form is typical for gold thin platy crystals; iii) gold is the most mobile

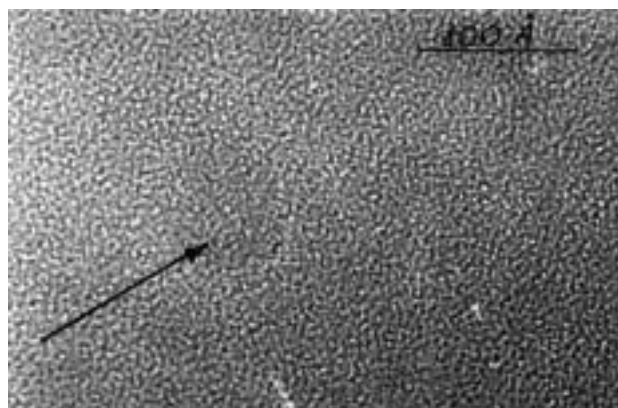


Fig. 6. HREM image of gold cluster (arrow) in silicate amorphous matrix.

element during quartz alteration, as Table 1 shows. The contrast peculiarities of HREM image make it likely to suggest that the cluster has a monoatomic thickness. Taking into account its size of 46 Å (17 atomic planes), the total number of gold atoms in this cluster may be estimated as about 150-200. Thus, invisible gold becomes visible and forms nuggets.

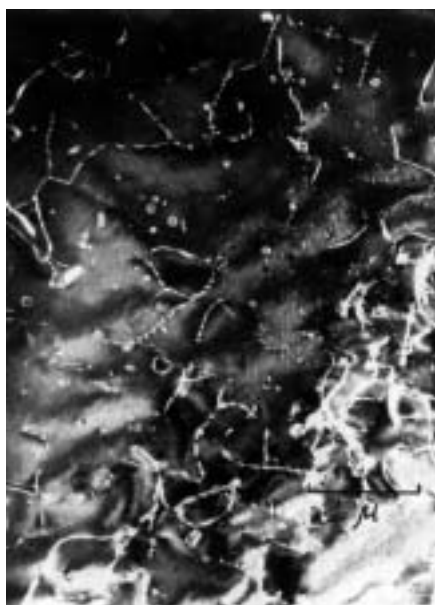
## 5. Discussion

Considered jointly, the results of AAS, IRS, TG, X-ray, TEM and HREM studies show that there is crystallochemical relationship among SiO<sub>2</sub>, H<sub>2</sub>O and trace elements within the quartz matrix. Au and Fe are more abundant in QuI than in QuII, and chemical analyses (Table 1) shows a positive correlation between them. Besides, there is experimental evidence of Au-Fe close tie within aquacomplex, presented in Fig. 1 [14]. Taking into account these cases, we concluded that like the classic  $\text{Na}^+\text{Al}^{3+} \rightarrow \text{Si}^{4+}$  scheme,  $\text{Au}^+\text{Fe}^{3+} \rightarrow \text{Si}^{4+}$  substitution is also possible. It means that Fe<sup>3+</sup> occupies Si<sup>4+</sup> position in [MeO<sub>4</sub>] - tetrahedra, while Au<sup>+</sup> as ion-compensator enters an interstitial position Me<sup>n+</sup> (Fig.1 a).

IRS, TG, X-ray, TEM data reveal that there is a rigid association between structural gold and molecular water. Structural molecular water is the major one in QuI; it is released at 650 °C that triggers crystallochemical rearrangements of the whole lattice, so the latter becomes more perfect and clean from growth dislocations and impurity defects. At the same time, new metallic phases and gas-fluid bubbles arise and become detectable in the silica matrix.

Such observations suggest the existence of the unit H-containing impurity complex defect similar to that given in Fig. 1a. This model explains the mechanism of structural chemical transformations up to a complete quartz amorphization under electron irradiation. As donor-acceptor bonds become saturated, H<sub>2</sub>O molecules leave their positions between [SiO<sub>3</sub>] and [Me<sup>n+</sup>O<sub>4</sub>] tetrahedra and form water clusters. After that Me<sup>n+</sup> cations (Au<sup>+</sup> here) leave their interstitial positions and segregate together in accumulations of about several tens of angstroms in size (Fig. 1b). This makes the strained QuI lattice perfect and free of defects. At the same time the model explains the

a)



b)



Fig. 5. TEM images of QuI (a) and QuII (b)



most important characteristics of H-containing quartz:  
 i) simultaneous presence both OH<sup>-</sup> and H<sub>2</sub>O forms on IRS spectra and the appearance of free water after heating that is not detectable initially; ii) association of H with different cations in H-related defects; iii) existence of both crystallographic and gel-like defects of complex composition; iv) amorphization of quartz, containing structural water; v) single crystalline structure of quartz with structural water.

## 6. Conclusion

A complex investigation of natural quartz from the veins with gold-sulfide mineralization supports the model for the complex silica-water-metal oxide defects, whose incorporation in SiO<sub>2</sub> matrix covers the variety of silica forms existing in nature. This result has both basic and applied aspects. The first one relates to solution of the problem of water speciation in quartz; the second one clarifies the nature of so called <<invisible>> gold in quartz. Comparative investigation of two contrasting quartz varieties: gray transparent QuI and milky sugar-like QuII shows how clustering of structural atomic gold into gold nuggets occurs during complex crystallochemical transformations of vein quartz.

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