MÖSSBAUER STUDY OF ALLANITE[1]

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A combination of Mössbauer spectroscopy and X-ray analysis was employed to study natural samples of allanite. In this contribution we will describe how the general shape of the Mössbauer spectra can be used to get information about the phase composition and cation distribution of iron in the crystallographic structure of allanite. The obtained information is then used to derive mineralogical and petrological conclusions.

Silicates are evidently the most important group of rock-forming minerals. They often crystallize as solid solutions at high temperatures in complex crystal structures having large unit cells of low symmetry. Because of their overwhelming presence and fundamental importance in agriculture, construction, and numerous industrial processes from cement to paper making, any physicochemical analysis will inevitably be used to refine our knowledge of the structure and properties of the bedrock on which life and culture are founded. Mössbauer spectroscopy has been no exception in this respect. The technique offers a view of the structure of minerals from an unusual perspective, the iron cation site and ferrous-ferric ratio.

The problem of identifying subspectra with specific sites in minerals is not a trivial one because most naturally occuring silicates are intermediate members of solid solution series, and therefore include both iron and other metallic cations distributed more or less at random over "equivalent" crystallographic sites. Iron environments are therefore all slightly different from each other, depending on the charge and radii of the neighboring cations.

Normally we are dealing with paramagnetic spectra of silicates, because it is rather unusual to find the minerals containing enough iron to order magnetically even in the liquid helium temperature range. Therefore some additional problem arising from cation disorder are present in the interpretation of the iron quadrupole doublets e.g. distribution of isomer shifts and quadrupole splitting [1].
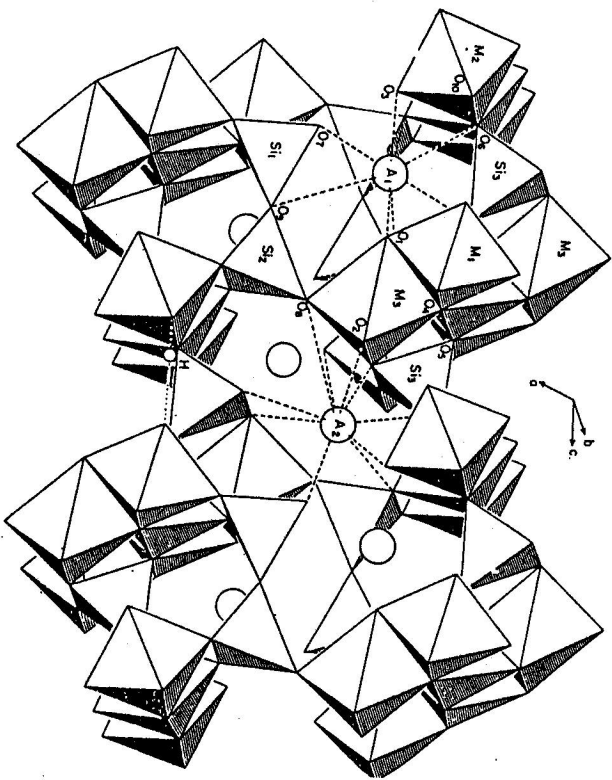
Fig 1. The structure of allanite

There exist only few papers concerning to application of Mössbauer spectroscopy on allanite and these are not in agreement in the number of crystallographic position of iron and in the parameters of individual subspectra [2].

The combination of the data obtained from Mössbauer spectroscopy, roentgen diffraction and chemical analysis allows us to find the distribution of Fe^{2+} and Fe^{3+} betwen four M1 and M3 positions in the crystallographic structure of allanite.

Of the minerals including isolated Si_2O_7 double tertrahedra, those of the epidotite group are the most common.

Allanite is a characteristic accessory mineral in many granites, granodiorites, monzonites and syenites, and occurs in larger amounts in some limestone skarns and in pegmatites [5]. The structure of allanite is similar to that of epidote and its generalized formula can thus be expressed as

$$(Ca\ RE)_2(Fe^{2+}, Fe^{3+})\ Al_2O \cdot OH\ [Si_2O_7][SiO_4]$$

where RE represent all (but mainly light) rare earth elements. Allanite has the same structure as epidote, but there is substitution of a large trivalent lanthanide ion for calcium which is usually balanced by replacement of some of the intrachain Al by Fe^{2+}. The Mössbauer spectrum should show four doublets assigned to Fe^{2+} and Fe^{3+} in M3 positions, and Fe^{2+} and Fe^{3+} substituting for in-chain aluminium in M1 sites [1].
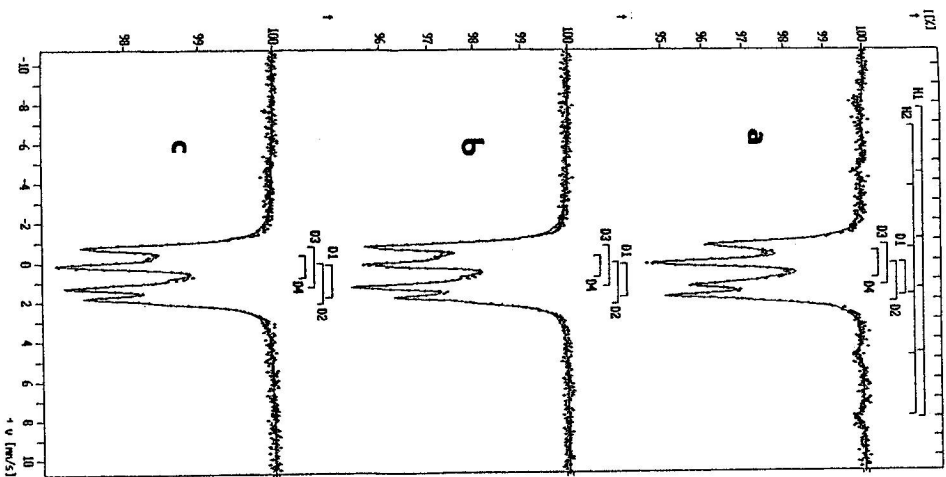
Fig 2. Mössbauer spectra at room temperature of the three allanite samples

The electrostatic balance is maintained by the substitution of Fe^{2+} for Fe^{3+}. The crystallographic structure of allanite is shown in Fig.1 adapted from [4].

The crystallographic properties of the samples were studied by use of Mössbauer spectroscopy. The spectra were obtained using a constant-acceleration Mössbauer spectrometer with a source of ^{57}Co in Rh matrix. Figure 2 represents spectra obtained at room temperature. In the spectrum of sample "A1" (Fig.2a) a small amount of magnetite pattern (H_A, H_B) was detected. The association of allanite + magnetite is common in the studied rock type, see below.
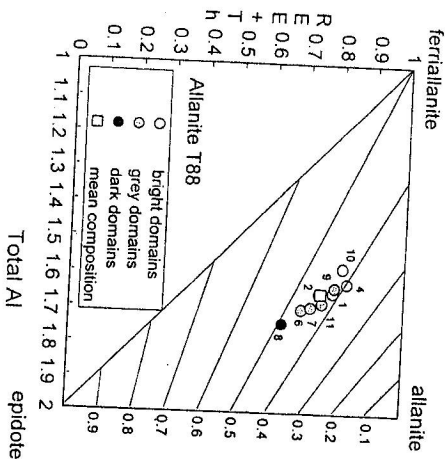
ferri-allanite

Allanite T88

○ bright domains
● grey domains
□ mean composition

Total Al   epidote

allanite

Fig.3 Total REE + Th vs. Al diagram for allanite (a) showing three allanite end- members and isolines of F ratio ($=Fe^{3+}/(Fe^{3+} + Fe^{2+})$). Small numbers refer to individual spot analyses, the square is mean composition with Mössbauer derived F. See text for details.

ferri-allanite

Allanite ZK-83

○ bright domains
● grey domains
□ dark domains
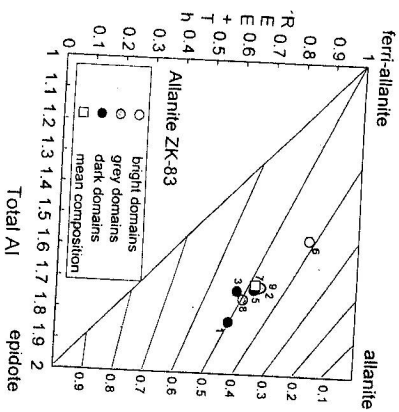   mean composition

Total Al   epidote

allanite

Fig. 4 Total REE + Th vs. Al diagram for allanite (b) Explanations as in Fig. 3.

The doublet D1 represents ferrous iron in M3 positions and its relative content is 41.5% . In the M1 positions doublet D2 is 7.5% of Fe^{2+}. The total amount of ferric
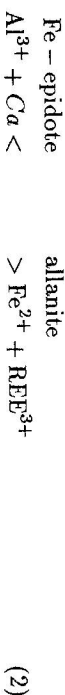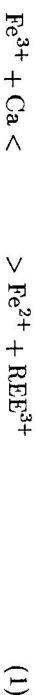
Table 1. The results of computer analysis of Mössbauer spectra

S.	D1			D2			D3			D4		
	IS $\frac{mm}{s}$	QS $\frac{mm}{s}$	%	IS $\frac{mm}{s}$	QS $\frac{mm}{s}$	%	IS $\frac{mm}{s}$	QS $\frac{mm}{s}$	%	IS $\frac{mm}{s}$	QS $\frac{mm}{s}$	%
A1	0.97	1.65	41.5	1.10	1.92	7.5	0.26	2.00	36.5	0.24	1.07	9.0
A2	0.97	1.65	33.4	1.10	2.07	8.7	0.26	1.98	45.1	0.26	1.01	12.8
A3	0.97	1.64	36.0	1.07	2.00	10.8	0.26	1.99	46.1	0.25	1.10	11.1

iron is 45.5% from which 36.5% in M3 positions (doublet D3) and 9.0% in M1 positions (doublet D4). The rest of iron (5.5%) is in magnetite. The Mössbauer data thus indicate rather high Fe^{3+} content ranging between 30-40 at.% which is shown below to be consistent with published data for high temperature magmatic allanites. By contrast, low temperature, hydrothermal and metamorphic allanites show, respectively, higher and lower Fe^{3+} contents [6].

The presence of magnetite was not observed in the spectra of the other two samples (Fig.2 b,c). The highest Fe^{3+} content of the allanite (c) probably reflects the presence of epidote, abundant in this sample, typically overgrowing the allanite grains. The quantitative data of the computer analysis for all samples are summarized in Table 1. The isomer shift values are given with respect to Rh.

Allanite is a characteristic accessory mineral of granitic rocks of the Western Carpathians (which build the Slovak territory) typically occuring in the assemblage with magnetite [6 and citations therein]. We have studied 3 samples of allanite from the Sihla tonalite, a major granitoid type of the Paleozoic basement. Allanite here shows a complicated internal structure consisting of a patchwork of irregular domains with differing atomic number. A detailed study of SCAN backscattered images enabled to interpret the darker domains as secondary allanite, formed during late magmatic stages due to interactions with high temperature fluids [6]. Two of the studied allanites (A1,A3) were analysed by X-ray microanalysis (more than 20 spot analyses) for 15 samples including 6 rare earth elements (REE). Examination of substitution relations confirmed the two main substitutions [3, 4]:

$$Fe^{3+} + Ca < \quad > Fe^{2+} + REE^{3+} \quad (1)$$

Fe − epidote   allanite

$$Al^{3+} + Ca < \quad > Fe^{2+} + REE^{3+} \quad (2)$$

Fe − epidote   ferriallanite

As only few authors report both FeO and Fe_2O_3 in their allanite analyses, a plot was proposed by Petrik et al. [6] contoured for the ratio $F = Fe^{3+}/(Fe^{3+} + Fe^{2+})$; total REE vs. Al. This ratio is unique for the allanites controlled by substitutions (1, 2) and enables, therefore, the amount of trivalent iron to be estimated in microprobe analyses reporting only FeO total. A direct comparison with Mössbauer derived F ratios (Table

1) shows that the plot distinguishes between more oxidized allanite (ZK-83 - sample A3) and less oxidized allanite (T88 - sample A1). This is illustrated in Figs. 3, 4 where squares refer to mean allanite compositions recalculated to 12.5 oxygens and Fe divided according to Table 1. The circles refer to spot microanalyses with shades corresponding to observed brightness in backscattered images. The spot analyses have FeO divided according to stoichiometric, charge-balance criterion per 25 negative charges (e.g.[7]). The plot (Figs. 3, 4) clearly shows that dark patches are oxidized domains where the escape of part of REE is compensated by the increase of F ratio. However, the examination of a number of published allanite microprobe analyses (not shown) revealed that igneous (magmatic) allanites maintain their F ratio within a narrow limit: 0.4 ± 0.05 [6]. This suggests that igneous allanites were buffered during crystallization from granitic magmas, possibly through equilibrium with biotite at relatively oxidizing conditions with oxygen fugacities corresponding to buffers Ni-NiO or titanite- magnetite- quartz-amphibole [6].

The cation distributions as determined from the Mössbauer spectra are in good agreement whith those obtained from the proposed crystallographic structure and with the data given in the literature [4, 6].

It has been shown that for the various allanite minerals in principle it is possible to determine the following:

a) the charge of iron

b) its distribution in different sites in the same mineral

c) the iron-bearing minerals themselves

Allanite is a sensitive indicator of redox conditions in magmas and typically preserves parts of its original compositions along with altered (oxidized) domains. The preserved parts with roughly 40 at.% of Fe^{3+} of total Fe indicate rather high oxygen fugacities in acidic magmas during precipitation from melt. Secondary domains, in turn, reflect the role of fluids in increasing of redox conditions during late - to postmagmatic stages.

We can conclude that the combination of Mössbauer spectroscopy with other methods of investigation (X-ray microanalysis, backscattered electron imaging) gives us invaluable information which can help to solve particular mineralogical and petrological problems.

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