

ELECTRON PARAMAGNETIC RESONANCE (EPR) SPECTROSCOPY OF NEPHRITE (FROM NEOLITHIC ARTEFACTS FROM SW BULGARIA)

Ruslan I. Kostov

University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; rikostov@yahoo.com

ABSTRACT. Electron paramagnetic resonance (EPR) studies are carried out in different regimes on five samples of nephrite $\square\text{Ca}_2(\text{Fe,Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ from Neolithic artefacts, found during archaeological excavations in prehistoric settlements in South-West Bulgaria – Galabnik, Bulgarchevo and Kovachevo. Three types of signals are identified in the EPR spectra of the studied samples of nephrite. The first one is a weak signal of Fe^{3+} (with a $g \sim 4.3$; in supposed tetrahedral sites in the structure), the second one is a strong and broad signal due to iron-bearing phases and/or Fe^{3+} - Fe^{2+} clusters (with $g \sim 2$) and the third one – a signal from Mn^{2+} (6-component signal at $g \sim 2$ with a wide of ~ 50 mT). The EPR spectroscopic data as well as the geochemical data are considered as useful for determination of groups of nephrite samples from one, two or more probable deposits (occurrences) on the territory of Southern Bulgaria or some other Balkan countries.

ЕЛЕКТРОНЕН ПАРАМАГНИТЕН РЕЗОНАНС (ЕПР-СПЕКТРОСКОПИЯ) НА НЕФРИТ (ОТ НЕОЛИТНИ АРТЕФАКТИ ОТ ЮГОЗАПАДНА БЪЛГАРИЯ)

Руслан И. Костов

Минно-геоложки университет "Св. Иван Рилски", 1700 София; rikostov@yahoo.com

РЕЗЮМЕ. Проведени са изследвания чрез електронен парамагнитен резонанс (ЕПР) в различен режим на 5 проби нефрит $\square\text{Ca}_2(\text{Fe,Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (от неолитни артефакти, разкрити при археологически разкопки от праисторически селища в югозападна България – Гълъбник, Българчево и Ковачево). Три типа сигнали се установяват в ЕПР спектрите на изучените проби от нефрит. Първият е слаб сигнал от Fe^{3+} (с $g \sim 4.3$; във вероятно тетраедрични позиции в структурата), вторият е силен и широк сигнал, дължащ се на желязо-съдържащи фази и/или Fe^{3+} - Fe^{2+} кластери (с $g \sim 2$) и третият сигнал се дължи на Mn^{2+} (6-компонентен сигнал при $g \sim 2$ с ширина от ~ 50 mT). Данните от ЕПР спектроскопските изследвания, както и геохимичните такива, се приемат като полезни за определянето на групи нефрит от едно, две или повече възможни находища (проявления) на територията на южна България или някои съседни балкански страни.

Nephrite $\square\text{Ca}_2(\text{Fe,Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ is a Fe-Mg-bearing Ca-silicate mineral with double-chain structure in the group of amphiboles. It is a massive fine fibrous member with a composition in the tremolite $\square\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ - ferroactinolite $\square\text{Ca}_2\text{Fe}^{2+}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ amphibole series. Usually nephrite has a tremolite to actinolite composition (for the structure, composition and elementary cell parameters, compare Hawthorne, 1981; Leake et al., 1997; Verkouteren, Wylie, 2000; Hawthorne, Oberti, 2007). It is recognized mainly with a pale green or dark green colour, but can also be white, yellowish or brownish depending of the presence or lack of isomorphic or phase impurities (Kostov, 2003). Some rare bluish black nephrites from the alkaline Murun Massif in the Russian Federation have been also described, with a composition in the richterite-arfvedsonite amphibole series (cited after Bakhtin et al., 1997).

Nephrite and jadeite ($\text{NaAlSi}_2\text{O}_6$, another similar in colour, pale coloured greenish mineral from the group of pyroxenes) are frequently mistaken in general archaeological or popular articles, and the unified term "jade" has been introduced a long time ago, when no precise mineralogical determination has been used. Jadeite has hardness on the Mohs's scale 7-6.5,

and nephrite – 6-5.5. This gem material has been esteemed by a lot of prehistoric and ancient cultures because of the toughness of the mineral due to its internal structure. The mineral crystallizes in the monocline-prismatic class of the monoclinic system forming aggregates composed by fine interlocking fibers (Mallinson et al., 1980; Dorling, Zussman, 1985; Kovalenko et al., 1985).

The nephrite aggregates have a specific grain-like to fibrous fracture. Its specific gravity is in the range 2.9-3.1. Its luster is glassy to greasy. Nephrite is optical biaxial (negative) mineral, and the refractive indices are among 1.600-1.614 and 1.627-1.641. It posses a marked dichroism (the green colour becoming yellowish), masked by the fine fibres. According to structure, several types of nephrite aggregates can be distinguished – massive, spotted, layered, and with adopted from the serpentines black inclusions of oxide mineral phases. In most cases, the nephrite aggregate is not transparent, but translucent in thin slices. The genetic types of nephrite deposits have been described in numerous monographs and special papers in gemmology (see Ostrovskaya, 1981; Suturin, Zamaletdinov, 1984; Harlow, Sorensen, 2001; Kostov, 2003). They can be attributed mainly to two genetic types, related to

serpentinites and to carbonate rocks. In the first case nephrite associates with quartz-zoisite-albite and/or diopside-tremolite mineralization, and in the second case – with contact metasomatic zones in carbonate rocks (marbles).

Nephrite artefacts are known from prehistoric sites in Bulgaria since the Early Neolithic and they disappear at the end of the Chalcolithic period (Kostov et al., 2003; Kostov, Bakamska, 2004; Kostov, Genadieva, 2004; Kostov, 2005a; 2005b; 2007a; 2007b; Kostov, Lang, 2005; Kostov, Machev, 2007). The nephrite source is under discussion as no nephrite deposits (occurrences) have been reported on the Balkans. The wide distribution of this gemmological material and its use for prestigious and attractive artefacts (Nikolov, 2005) during the mentioned prehistoric periods gives the opportunity for searching of local sources on the territory of southern Bulgaria and neighbouring countries on the Balkans where there is a suitable for nephrite formation geological setting with a lot of serpentinised ultrabasic rocks outcrops. Because of their abundance, fine design and most early appearance in Europe and worldwide, the nephrite artefacts are related to a newly introduced prehistoric Balkan “nephrite culture” in analogy to the later in age Chinese “nephrite cultures” (Kostov, 2005b).

The chemical compositions of the nephrite artefacts from some of the Neolithic sites in Bulgaria are close (Kostov, 2007a; 2007b; N15-17). The high FeO content in some analyses will transfer the nephrite from the field of tremolite in the field of actinolite (Leake et al., 1997; for chemical analyses see Letnikov, Sekerin, 1983; Hung et al., 2006). For a more precise structural and chemical identification of some structural defects in nephrite, five samples are studied by electron paramagnetic resonance (EPR; or electron spin resonance in some publications, ESR) spectroscopy.

EPR spectra are recorded on a JEOL FA100 facility in the X-band (9.5 GHz; with standard conditions of the EPR spectra at a microwave power of 0.998 mW, modulation 100 kHz, time constant 4 and 8 minutes for different range of the corresponding magnetic field) at room temperature. The EPR spectra are recorded at different position of the magnetic field – 500 mT for eventual detection of broad signals and identification of the Fe^{3+} signal at $g=4.3$ and 100 mT for identification of electron-hole centers and trace elements in the $g=2$ region, where appears the 6-component signal of Mn^{2+} .

For the EPR studies 5 samples of nephrite from artefacts were chosen, all of them found in prehistoric sites along the Struma River valley in South-West Bulgaria (previously analyzed by electron microprobe analyses; Kostov, 2007a; 2007b): one sample from Bulgarchevo (fragment of an axe from the south pit; B1, pale green, N870), two samples from Galabnik (fragments of small axes; G1 – pale green, N92/330; G2 – dark green, without number) and two samples from Kovachevo (fragments of small axe or wedge; K1 – pale green, N54499/2001; K2 – dark green, N46203/1999). The artefacts from Galabnik and Kovachevo are from the Early Neolithic and the sample from Bulgarchevo – probably from the Late Neolithic. For the EPR spectroscopy study a volume of 5-7 mm³ material has been placed in a small quartz tube.

According to previous EPR studies in tremolite are identified paramagnetic centers Mn^{2+} (Bershov et al., 1966; Marfunin et

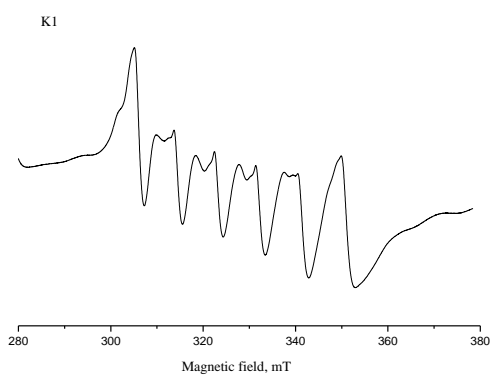
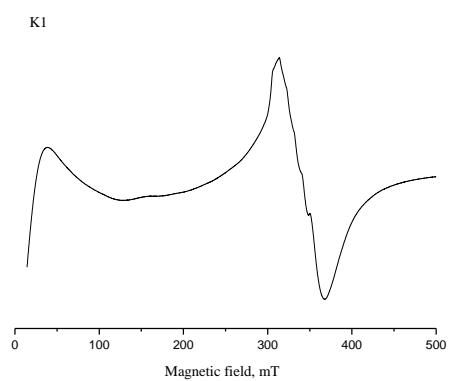
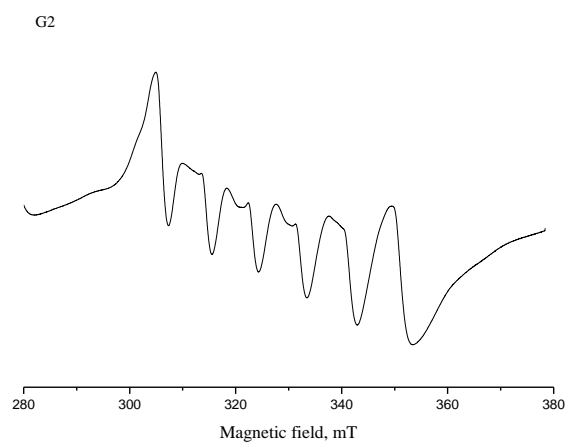
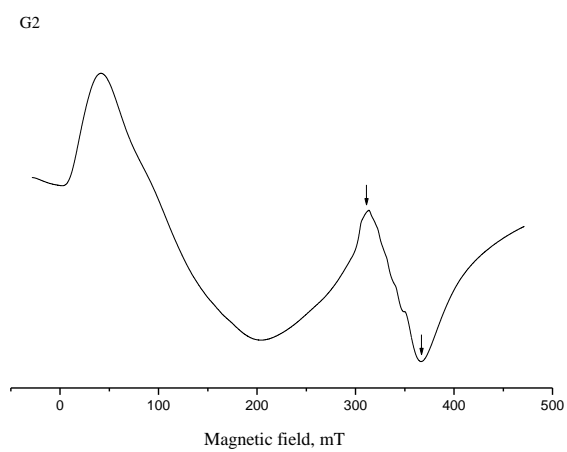
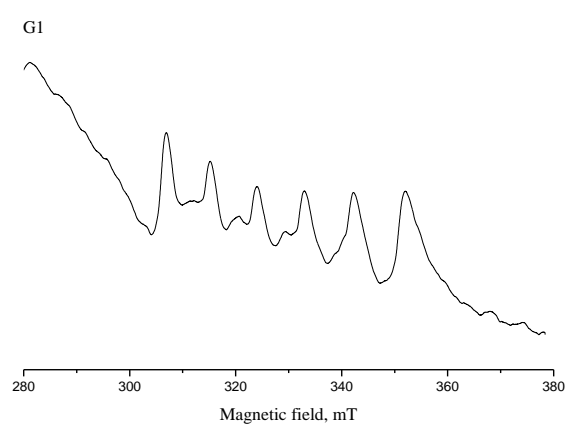
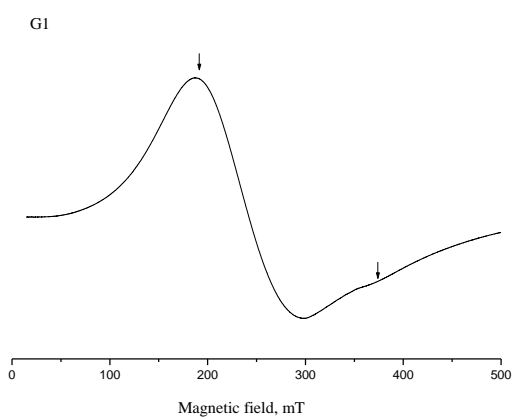
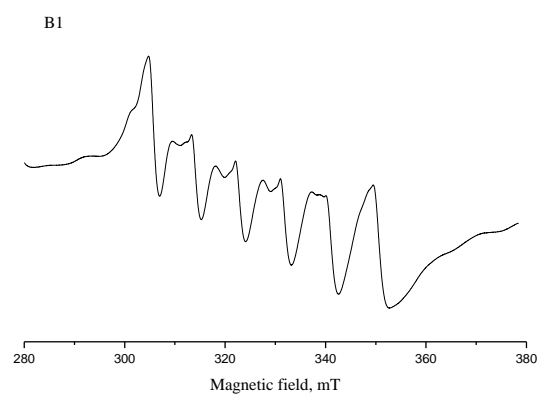
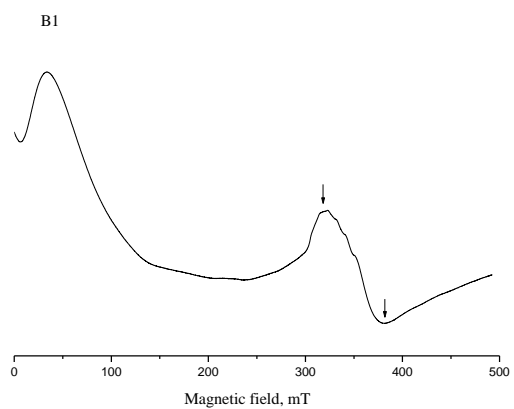
al., 1966; Manoogian, 1968; Golding et al., 1972; McGavin et al., 1982; Craighead Tennant et al., 2007; according to optical spectroscopy data – Bakhtin et al., 1979; Bakhtin, 1985), Fe^{3+} (McGavin et al., 1984; Craighead Tennant et al., 2007) and phosphorus-bearing groups (Bershov, 1970), and in actinolite – Mn^{2+} and Fe^{3+} (Gopal et al., 2004) (for reviews with data on tremolite-actinolite see Calas, 1988; Vassilikou-Dova, 1993). In the EPR spectra of amphibole also have been registered several other centers with a g -factor value about 2, all of them with a suggested hole nature (Matyash et al., 1980).

Three types of signals are identified in the EPR spectra of the studied samples of nephrite from Neolithic artefacts (Fig. 1). The first one is a weak signal of Fe^{3+} (with $g\sim 4.3$; in tetrahedral sites in the structure), the second one – a strong and broad signal due to iron-bearing phases and/or Fe^{3+} - Fe^{2+} clusters (with $g\sim 2$ with a superimposed signal) and the third one – signal from Mn^{2+} (6-component signal at $g\sim 2$ with a wide of ~ 50 mT). In sample G1 a very strong broad signal is detected (~ 100 mT; shifted to $g\sim 3$) which is attributed most probably to numerous iron-bearing phase (this signal does not allow to identify other weaker signals from other paramagnetic centers).

Similar impurity centers are known in several minerals, as well as in natural glasses, including in perlitites from Bulgarian deposits (Kostov, Yanev, 1996). It is assumed, that the width of the signal at $g\sim 2$ in the case with the iron clusters corresponds to their size (Calas, Petiau, 1983). A weak EPR signal from Fe^{3+} is detected in both samples from the Kovachevo site. Such signal has been registered without comment (Manoogian, 1968), but later it has been attributed to high-spin Fe^{3+} in unclear structural sites (McGavin et al., 1982). A signal from iron-bearing microphases or Fe^{3+} - Fe^{2+} clusters is recorded in the spectra of all the samples with maximum intensity in the pale coloured sample from Kovachevo (K1).

The ion Mn^{2+} substitutes in the amphibole structure (with a tremolite to actinolite composition) both Ca^{2+} and Mg^{2+} , with a specific EPR spectrum (^{55}Mn ; spin 5/2; abundance 100%). The investigations in another band (Q; 94.1 GHz) display, that the well exposed six-component structure in the spectra is due to replacement in the structural position of Ca^{2+} by Mn^{2+} (McGavin et al., 1982; Craighead Tennant et al., 2007), and that is dominantly the position of the M_4 deformed polyhedron (Papike et al., 1969). In the studied samples Mn^{2+} has been registered in all the EPR spectra, even in those samples, where the element has not been detected by electron microprobe analysis. The arbitrary intensity of the EPR peaks corresponds to the manganese content – thus the EPR studies can be used for a quantitative or semiquantitative evaluation of the manganese impurity. It is in lower concentrations in the darker nephrite varieties (samples G2 and K2).

EPR data, especially for nephrite, are known published only for samples from New Zealand (Craighead Tennant et al., 2007) or for some sort of fibrous actinolite (Gopal et al., 2004). In both cases the EPR data are being correlated with data from other spectroscopic methods (the EPR spectra are similar to those, which are obtained from the Bulgarian samples).



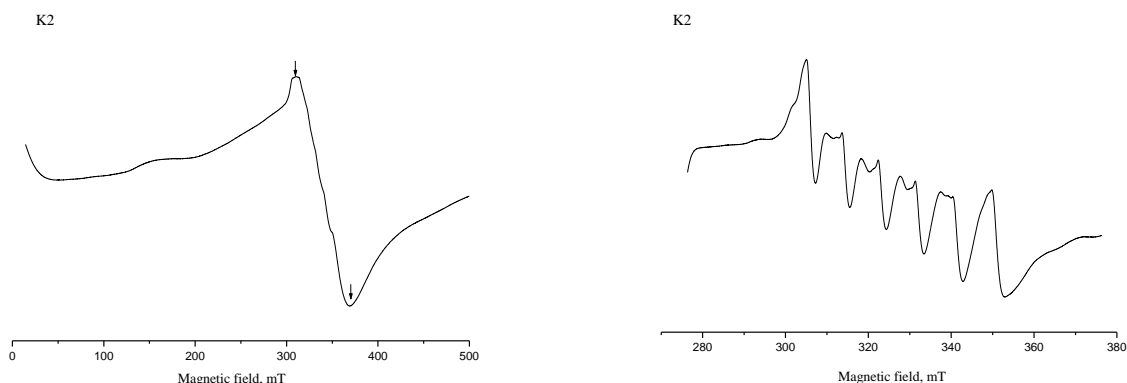


Fig. 1. ERP spectra of nephrite from Neolithic artefacts (left – width of the magnetic field 500 mT; right – width of the magnetic field 100 mT, the arrows show the range of the 6-component signal of Mn^{2+}): B1 – Bulgarchevo; G1 and G2 – Galabnik; K1 and K2 – Kovachevo (the same number of sample can be compared from their chemical analyses, Kostov, 2007b).

Attention has to be paid, during the EPR analyses of nephrite that the sample are not been contaminated with serpentine minerals (serpentine artefacts usually are close to nephrite artefacts in archaeological sites; Kostov, 2008), as according to EPR studies in antigorite one can be find the same impurities elements as Fe^{3+} (with g фактор ~ 4.3) and Mn^{2+} (six lines at $g \sim 2$; width 92.5 G) (Reddy et al., 2001).

According to Mössbauer spectroscopy data of pale green and dark green nephrites, it has been found that the spectra for tremolite and actinolite are practically identical, in both cases with two quadruple doublets from ions Fe^{2+} in two non-equivalent octahedral positions – the inner doublet of Fe^{2+} in M_2 sites, and the outer doublet correspondingly to Fe^{2+} in the M_1 and M_3 sites (Platonov et al., 1975; Sutura, Zamaletdinov, 1984). According to some other data (Wilkins, 2003; Craighead Tennant et al., 2007) the inner doublet corresponds to Fe^{2+} in the M_4 sites.

The position of the iron ions is registered by Mössbauer spectroscopy (Burns, Greaves, 1971; Craighead Tennant et al., 2007; general data for the amphiboles compare in Matyash et al., 1980) and that of the Mn^{2+} (bands at 570 nm in the position of Ca^{2+} and at 620 nm in the position of Mg^{2+}), Cr^{3+} (690-700 nm) and Fe^{3+} (720-730 nm), rarely the center O- (450-500 nm) by X-ray luminescence data (together with thermoluminescence) of nephrites (Boroznovskaya et al., 2007). It has been stressed, that among the green nephrites of a serpentinite origin the X-ray luminescence decreases in the presence of Fe^{2+} , and among the pale coloured nephrites from the carbonate rocks an intensive X-ray luminescence of Mn^{2+} and Cr^{3+} both is detected.

During the study of the optical spectra of nephrites from different deposits in general are obtained bands in the regions 21000-24000 cm^{-1} (from Fe^{2+} in octahedral sites), 14000-16000 cm^{-1} (with a significant importance for the intensity of the green colouration) or bands of charge transfer from transitions between iron ions of different charge in different octahedral sites Fe^{2+} (M_1) \rightarrow Fe^{3+} (M_2) (in charge for the bluish tint in some nephrites) and 10000-11000 cm^{-1} (from Fe^{2+} in octahedral sites in geometrically non-equivalent sites in the structure) (Platonov et al., 1975). The three-charge iron can be detected in the optical spectra by the charge transfer bands O^{2-}

$\rightarrow \text{Fe}^{3+}$ with an increasing yellowish hue (for content over 1% Fe_2O_3), and the other important colouring agent – the ion Cr^{3+} has absorption bands with a complex nature about 14000-16000 and 22000-23000 cm^{-1} (Platonov et al., 1975). The colour of the studied nephrites from Russia and Kazakhstan varies in the region 507-576 nm, and the brightness – from 1.992 (dark gray) to 11.642% (white to a pale green colour), dominating being the samples in the range of the colour hue 545-565 nm and brightness 2.5-4% (Sutura, Zamaletdinov, 1984). The mentioned data for nephrite correspond to amphiboles of a tremolite to actinolite composition (Bakhtin, 1985). The absorption band at 415 nm, which has been identified among the rare dark bluish nephrites, corresponds to an electron transfer of Mn^{2+} in an octahedral site (in the amphibole structure this is mostly the M_4 site) (Bakhtin et al., 1997). The absorption bands at 520, 560 and 800 nm in a manganese-bearing tremolite (hexagonite) are related to ions Mn^{3+} in an octahedral M_1 , M_2 and M_3 site (Bakhtin, 1985).

The data from the microprobe analysis of the nephrite samples and of the oxide inclusions in them, as well as the content of the trace elements according to spectroscopic data point out that at least two different mineral deposits (occurrences) can be suggested for their origin. The samples from the Kovachevo site can be placed in one group and the samples from the Galabnik and Bulgarchevo sites – in a second one. Visually spotted nephrite prehistoric implements from other sites in Bulgaria (for example from the Neolithic site Kurdjali or the Chalcolithic site at Varna II) have not been studied, and in this respect at least one additional unknown type of nephrite deposit (occurrence) has to be suggested for search on the territory of Bulgaria or on the territory of the near to the border southern Balkan countries.

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