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Identification, Characterization and Properties of Apatites

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Additional information is available at the end of the chapter

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Abstract

The parameters of unit cell, structure, refractive index, solubility data, PO_4/CO_3 ratio, surface area, etc., are important parameters for characterization of phosphate rocks. Third chapter of this book introduces methods for identification, characterization and properties of apatites in four main sections. The first part describes techniques used for identification and investigation of properties of phosphate minerals, including X-ray diffraction analysis, powder neutron diffraction, X-ray fluorescence as well as spectroscopic and microscopic methods. Some of these techniques are then demonstrated on the fluorapatite specimen in the second part. The third part of this chapter deals with thermodynamic properties of apatite-type compounds and introduces some of thermodynamic predictive methods. The fourth part is dedicated to dissolution of apatite, where the reaction between solids and liquids according to different dissolution models is described. Chapter ends with methods for the evaluation of reactivity of phosphate rocks.

Keywords: Apatite, Carbonate to Phosphate Ratio, Dissolution of Apatite, Reactivity of Apatite, Citrate Solubility

3.1 Techniques used for identification of phosphate minerals

There are several parameters which are used in characterization of phosphate rocks, including the following [1],[2]:

- a. Unit-cell parameters
 - b. Refractive index
-

- c. Solubility data based on chemical extraction methods, e.g. neutral ammonium citrate solubility (NAC, **Section 3.4.3**)
- d. PO_4/CO_3 ratio as a measure of carbonate substitution in phosphate minerals
- e. Surface area and pore size distribution indicating the potential reactivity

The most important techniques used for the identification and characterization of phosphate minerals include methods for identification of phase composition, chemical composition, structure, surface properties, etc. A few often applied methods are introduced in this chapter [1],[2].

3.1.1. X-ray diffraction analysis

The diffraction of a beam of X-rays by a crystalline material is the process of beam scattering¹ by electrons associated with atoms in the crystal and of the interference of these scattered X-rays because of the periodic arrangement of atoms in the crystal and its symmetry.² X-ray diffraction analysis (XRD) is used for the determination of mineralogical composition and quantitative X-ray diffraction analysis (Rietveld method) for the refinements of structure of apatite from measured data using specialized software [3],[4],[5],[6].

Following the discovery of X-rays by RÖENTGEN³ [8],[10],[11] in 1895 and the proof that X-rays have the wave properties and diffract from a periodic atomic array by VON LAUE [12] and his students in 1912–1913, the analytical application of X-ray diffraction has developed slowly over the next 20 years. Most of the earliness efforts were aimed at the solution of crystal structures of common phases. DEBYE and SHEERER (1916) and HULL (1917) suggested that powder diffraction patterns could be used for the identification of quantification of crystalline compounds. However, because most of the early developments were directed toward solving single-crystal structures, it was really the middle 1930s when the powder diffraction method began to attract the follower with the publication of the procedure of HANAWALT and RINN and the database of patterns by HANAWALT, RINN and FREVEL (1938). With the conversion of data sets into the first set of the Powder Diffraction File in 1941, the phase identification applications expanded, and the modern counter diffractometer was developed by PARRISH, HAMACHER and LOWITZSCH [5].

The phase identification was one of the first applications to grow to useful level. Other major applications of diffraction analysis include following phase changes under nonambient conditions and atmospheres. The first diffraction experiments were actually done on single crystals. The method is primarily directed toward determining the crystal periodicity and symmetry and solving the arrangement of atoms in the material because this information is

¹ Scattering is the process where the beam of radiation or particles is deviated from its initial trajectory by the inhomogeneity in the medium which it transverses [7].

² Other kinds of radiation commonly used for diffraction analysis are neutrons (**Section 3.1.2**) and electrons (**Chapter 3.1.10**).

³ Wilhelm Conrad Röntgen (1845–1923) was the rector of the University of Würzburg [8]. The first X-ray photography was published in 1896 [9].

difficult to obtain from powder experiment. Powder diffraction is one of the most important material characterization techniques in the material research and industry [5].

Single-crystal diffraction studies are not limited to crystal structure analysis. The diffraction topography is a large field that has provided much information on the perfection of crystals used in industry as integral parts of devices. The examples include crystals used in sensing and control devices, substrates for electronic components, tools and dies, turbine blades and many other applications [5].

3.1.2. Powder neutron diffraction

Neutron powder diffraction (PND) or elastic neutron scattering enables to determine nuclear and magnetic structure of solids. Most of the information on the nature of ordered magnetic phases or magnetic structures comes from neutron diffraction experiments. Neutrons have no electric charge and interact with the nuclei rather than with the charge distribution of atoms in matter. They have the wavelength in the range of interatomic distances. They have magnetic moment and interact with the magnetic moment of atoms in matter. The mass of neutrons is similar to that of atomic nuclei; hence, they have energy and momentum similar to those of atoms in solid and fluid materials [13],[14]. The first neutron diffraction experiments were performed in 1945 by EO WOLLAN in the graphite reactor at Oak Ridge National Laboratory, USA [15].

Neutron scattering (NS) results from the interactions with atomic nuclei, i.e. overscattering lengths (distances) of the order of 10^{-15} m (1 fm).⁴ Although scattering amplitude decreases greatly with the scattering vector (it is inverse to the scattering length), there are insignificant variations of scattering amplitude in the same range of scattering vector for neutrons. Consequently, powder diffraction with neutrons can resolve very fine structural and textural details of complex atomic structures. Moreover, the weak interaction of neutrons with matter results in very low attenuation offering a unique advantage for nondestructive, in situ work and bulk analysis (for polycrystalline materials, no crushing is required to obtain the patterns) [14].

Neutron diffraction was used to determine atomic arrangement in material. Inelastic neutron scattering measures the vibrations of atoms and small-angle neutron scattering⁵ (SANS) is used to study larger structures such as polymers and colloids. The technique of surface reflection (reflectometry) was used to study layered materials. The technique of SANS provides the information about the size, shape and domain orientations; conformational changes and/or flexibility; and molecular associations in solution. For the structural studies, the elastic scattering effects, where there is no energy exchange between the radiation and atoms, are exploited [7],[14],[16].

Neutron powder diffraction is a method often used for the structure refinement of apatite or apatite type compounds from measured data using specialized software [17],[18],[19],[20],

⁴ The interaction with electrons during X-ray analysis takes place over the distances of 10^{-10} m (1 Å) [14].

⁵ Small angle scattering (SAS) of X-rays is abbreviated as SAXS [7].

[21],[22],[23],[24] and the effect of substitutions in the apatite structure [25]. Neutron diffraction data enable to explain the oxygen over-stoichiometry in the structure of $\text{La}_{9.67}(\text{SiO}_4)_6\text{O}_{2.5}$ apatite [17]. Since neutrons make possible the accurate determination of the thermal factors and provide the visualization of the diffusion paths in ionic conductors, powder neutron diffraction is also used for the characterization of solid oxide fuel cell materials [26]. This method is also used to investigate apatite in hard tissues where it provides the evidence about the deficiency of hydroxyl ion in bone apatites [27] and reconfirms that the inorganic portion is basically a hydroxylapatite-like material [27],[28].

3.1.3. X-ray fluorescence analysis and total-reflection X-ray fluorescence analysis

X-ray fluorescent analysis (XRF) is a method for the determination of sample composition [29], [30]. The origin of characteristic X-ray spectra can be described as follows. When sufficient energy is introduced into the atom, the electrons may be knocked out of one the inner shells. The atom is then in an excited (ionized) state and returns to the ground state within 10^{-8} s. The place of the missing electron is filled by an electron from a neighboring other shell, the place of which, in turn, is filled by an electron from more outer shell. The atom then returns to the ground state in steps. In every step, i.e. in every electron jump, the electron from a higher energy level goes into a lower energy level emitting excess energy in the form of an X-ray quantum. The energy of emitted radiation is characteristic for the atomic number of emitting element as well as for particular electron transition taking place within the electron shell of the atom. By measuring the energy or the wavelength of emitted radiation, the particle element can be identified unambiguously [31].

The energy that is necessary for the atom to get to excited state can be introduced either by the collision with a high-energy electron (sample is bombarded by electrons which are accelerated by high-voltage) or by the absorption of an energy-rich photon, i.e. the X-ray quantum (sample is irradiated by X-ray or gamma rays). In modern X-ray fluorescence analysis, the sample is irradiated by polychromatic radiation from an X-ray tube. In analogy to the optical case, this technique is referred to as fluorescence, which is responsible for the name X-ray fluorescence analysis as the technique of spectrochemical analysis with X-rays [31].

There are two types of instruments (**Fig. 1**) used for X-ray fluorescence spectrometry [32],[33]:

1. **Wavelength-dispersive XRF (WDXRF) or total reflection XRF (TRXRF):** the method is also often abbreviated as XRF. X-rays impinge on the sample (**Fig. 1(a)**) and generate fluorescent X-rays. These are then diffracted on a crystal. A goniometer selects the geometry between the crystal and detector that controls the detection of X-ray from the element of interest. Different crystals have different sensitivities. Many of commercial WDXRF instruments have two detectors and up to six crystals to optimize the conditions for each element.
2. **Energy-dispersive XRF (EDXRF):** the method is also abbreviated as EDX. The EDXRF instruments use much less energetic X-ray tube. Emitted X-ray radiation from the sample impinges directly on a detector, typically Si(Li), which generates pulses on an incident beam. These pulses are sorted and counted by a multichannel analyzer (**Fig. 1(b)**).

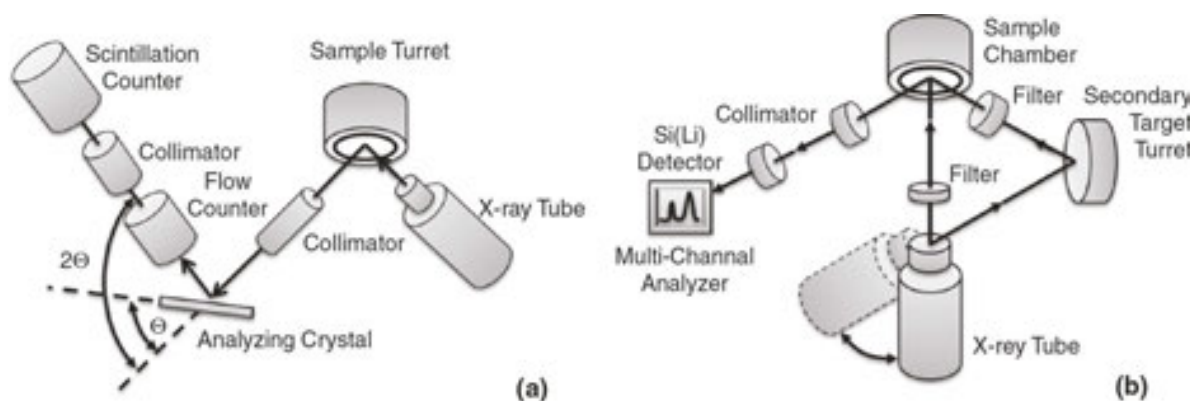


Fig. 1. Schematic representation of X-ray fluorescence analyzer: (a) wavelength-dispersive (XRF) and (b) energy dispersive (XRF).

Simultaneous determination for all elements, the atomic number of which is greater than Mg is possible.

The resolution and sensitivity of EDXRF is typically an order of magnitude worse than that for WDXRF.

Synchrotron radiation X-ray fluorescence (SRXRF) microprobe, a promising technique, is a nondestructive and qualitative to semiquantitative analysis of minerals and single fluid inclusions [34]. Synchrotron radiation (SR) is a powerful advanced light source (synchrotron radiation source, SRS) compared to conventional X-ray tube radiation and has many unique properties, such as high intensity, natural collimations, well-defined polarization, wide spectral range and energy tenability [35]. SRXRF is a widely applied technique for microscopic analysis of chemical elements. High-resolution requirements can be achieved using microbeam synchrotron radiation X-ray fluorescence (μ -SRXRF). Synchrotron radiation X-ray fluorescence can also provide the information about the oxidation state and coordination environment of metals using techniques known as X-ray absorption of near-edge structure (XANEX) or by micro-XANEX spectroscopy [37]. The unique tool for studying, the local structure around selected elements is X-ray absorption fine structure (XAFS) [38].

X-ray fluorescence is usually used to investigate the composition of apatite rocks and minerals for the purpose of their characterization [36],[39],[40], estimation of naturally occurring radionuclides in fertilizers [41] and analysis of phosphate ore at various stage of processing [42], e.g. flotation [43],[44].

3.1.4. Inductively coupled plasma spectrometry

Prior to inductively coupled plasma⁶ (ICP), the flame, direct current-arc and controlled-waveform spark were used for the atomization (i.e. decomposition of sample to individual

⁶ Plasma is defined as an electrically neutral gas which consists of positive ions and free electrons. Plasma have sufficiently high energy to atomize, ionize, and excite virtually all elements in the periodic table, which are intentionally introduced into it for the purpose of elemental chemical analysis [45].

atoms) and excitation of sample in elemental analysis. ICP denotes the technique that uses atmospheric pressure argon inductively coupled plasma⁷ (ICP) for the atomization and excitation of sample. This plasma is a highly energetic media consisting of inert ionized gas with equivalent temperatures from 7000 to 10,000 K. Inductively coupled plasma are formed by coupling energy produced by RF generator (typically 700–1500 W) to the plasma support gas with an electromagnetic fields [45]. The cross-section of typical ICP torch is shown in Fig. 2.

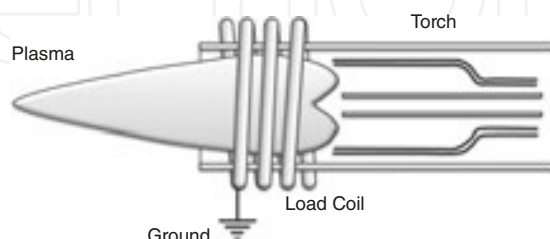


Fig. 2. Plasma with torch assembly and load coil [45].

The treatment of sample before the quantification includes vaporization, atomization, excitation and ionization.⁸ The introduction of analyzed sample into inductively coupled plasma was applied in analytical techniques including [29],[45],[46],[47],[48]:

- i. **Inductively coupled plasma atomic emission spectroscopy (ICP-AES):** the method connects atomic emission spectrometry with ICP. AES is based on spontaneous emission of free atoms or ions when the excitation is performed by thermal or electric energy. The method can identify and determine the concentration of up to 40 elements simultaneously with the detection limit of parts per billion (ppb). Serious limitations of this technique are the spectral interferences. Despite rapid growth of ICP-MS, ICP-AES still plays a dominant role in elemental analysis of geological, environmental, biological and other materials.
- ii. **Inductively coupled plasma atomic fluorescence spectroscopy (ICP-AFS):** ASF is an analytical technique for the determination of elements in small quantities. It is based on the emission of free atoms when the excitation is performed by radiation energy.
- iii. **Inductively coupled plasma-mass spectroscopy (ICP-MS):** is analytical technique for the determination of elemental composition of virtually any material. A sample, usually in the form of an aqueous solution, is converted to an aerosol by a neutralization process and transported to the plasma by an argon gas stream. In the plasma, the elements of analyte are atomized, followed immediately by ionization. The composition of ion population in the plasma is proportional to the concentration of

⁷ Although there are many types of plasma, such as direct current, microwave induced, etc., the ICP is considered the most useful technique for analytical spectroscopy [45].

⁸ Each element has characteristics first and second ionization potential, which depends on specific electronic structure of given element. Higher ionization potential means that more externally applied energy is required for ionization (thermal radiation, collision with other ion or electron, or exposure to high-energy photons) [45].

analyte species in original sample solution. Ions produced by ICP are representatively sampled and extracted from the plasma; next they are separated and measured by a quadrupole or time-of-flight mass spectrometer

The method known as laser ablation—inductively coupled plasma—mass spectrometry (LA-ICP-MS) is a coupling technique of laser ablation with ICP-MS technique [49],[50],[51],[52],[53]. Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) was applied as the benchmark method for isotopic analysis [54] and for the determination of heavy rare earth elements in apatites [55],[56],[57].

3.1.5. Thermal ionization mass spectroscopy

Thermal ionization mass spectroscopy (TIMS) is highly specialized technique of mass spectroscopy used for very precise determination of isotope ratios and, as such, is widely used for the determination of stable isotope ratios in isotope geology and for the analysis of nuclear materials [58]. In this method, the solid sample is thermally ionized in solid-source mass spectrometer. Ions are accelerated into the mass analyzer and then transported to the detector [59]. Multicollector thermal ionization mass spectrometry (MC-TIMS) uses laminated magnetic sector fillet for high speed peak jumping and low hysteresis for the mass of ion beams [60],[61].

The basic variants of the method of thermal ionization mass spectroscopy are as follows:

1. Isotope dilution–thermal ionization mass spectrometry method (ID-TIMS) [62],[63] is used for accurate determination of element concentration and is generally considered to be the definitive method to other techniques [58]. The method was applied for direct measurement of uranium, thorium, lead, etc., concentrations in the determination of single grain fission-track ages (**Section 7.3.3**).
2. Chemical abrasion–thermal ionization mass spectrometry method (CA-TIMS)

The ability for precise determination of isotope ratio in apatite predetermines this method for geochronological investigations, i.e. studying of chronologic records in accessory minerals of igneous rocks [61],[63],[64],[65].

3.1.6. Secondary ion mass spectrometry

Secondary ion mass spectroscopy (SIMS) is a method⁹ for the characterization of solid surface elemental composition and isotope distribution. The technique can be applied to all elements and allows quantitative analysis of solid surfaces, including monolayers. Energetic ion bombardment of a solid surface (primary ions, e.g. Ar^+ , Cs^+ , O^{2+} , ...) causes that atoms of the sample are shifted from their original states as positive and negative ions which are termed as secondary ions. These ions are then analyzed by mass spectrometer (e.g. quadrupole mass spectrometer) to determine the composition of the surface of sample [66],[67]. The applica-

⁹ The method was originally developed in the 1950s and 1960s by HERZOG et al and HONIG et al to analyze metals and oxides [69], but the basis of SIMS can be traced back to the beginning of the twentieth century with the first experimental evidence of secondary ions given by JJ THOMSON in 1910 [68].

tions of SIMS can be broadly subdivided into static and dynamic SIMS. Static SIMS (SSIMS) is used to investigate the composition of the outermost monolayer on any solid. Dynamic SIMS (DSIMS) examines the concentration profile as the function of depth [68],[69],[70].

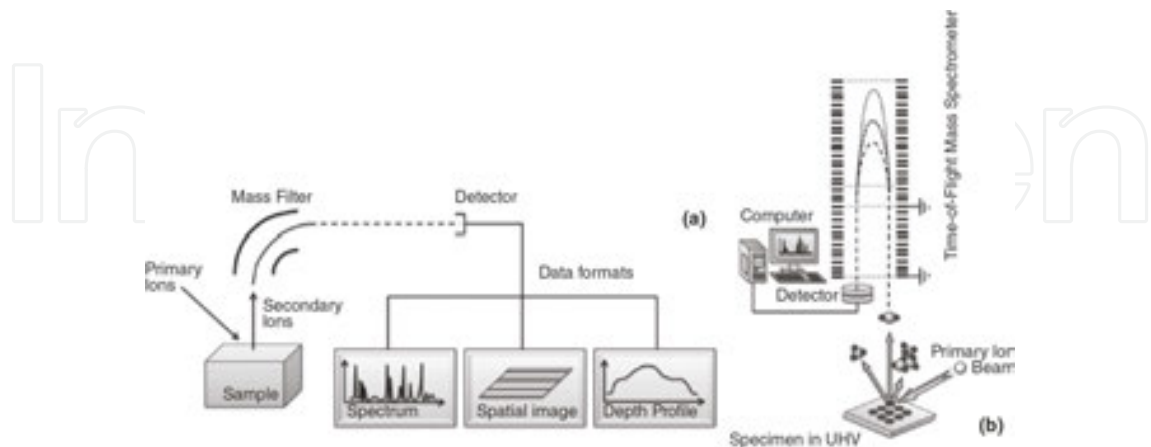


Fig. 3. Main components of SIMS [68] and schematic representation of ion microprobe imaging time-of-flight secondary ion mass spectrometry with reflectron-based mass analyser [69].

The mass filter of mass spectrometer of SIMS instruments defines the type of instruments [68], [70]:

1. Magnetic sector SIMS (M-SIMS) instruments (**Fig. 3(b)**, similar to those used in original mass spectrometer)
2. Quadrupole SIMS (Q-SIMS) instruments (**Fig. 4(a)**, first appeared in the 1970)
3. Time-of-flight SIMS (ToF-SIMS) instruments (**Fig. 4(b)**, first appeared in the 1980)

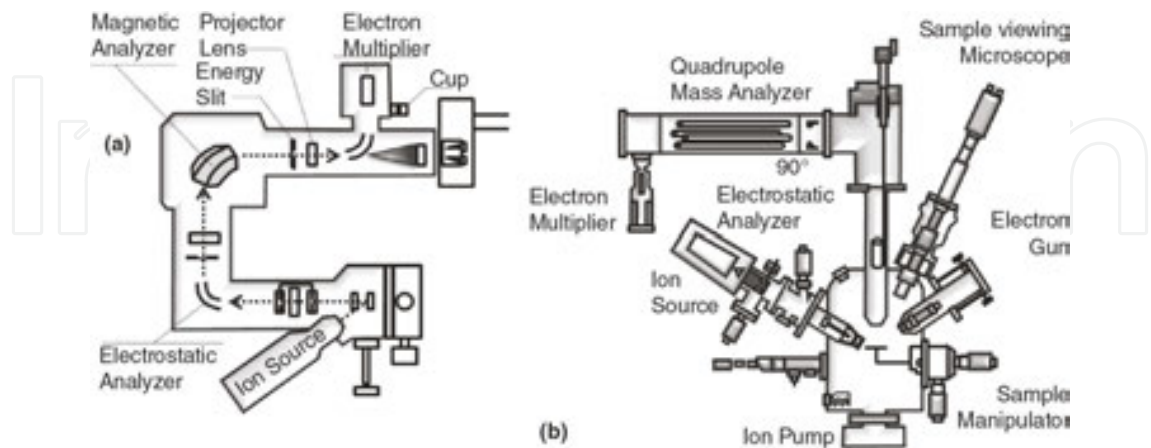


Fig. 4. Schematic representation of magnetic sector and quadrupole SIMS instruments [70].

Secondary ion emission begins when the primary ions energy exceeds some threshold level. This energy ranges from 30 to 80 eV and is much higher than the energies for sputtering of

neutral particles. The most important features of the method are very low sensitivity limit for majority of elements, the possibility to determine the concentration profile, the possibility of isotope analysis and the identification of all the elements and isotopes starting from hydrogen [66].

The SIMS method is often used for the measurement of deuterium/hydrogen (D/H) ratio and hydroxyl (OH) content in anhydrous minerals and melt inclusions in Martian meteorites [71] and lunar materials (apatite grains, glass beds, melt inclusions and agglutinates in soils) [72]. The method is widely used to investigate biological apatites and collagen apatite composites [73] and the analysis of micrometer-sized samples like, e.g. interplanetary dust, presolar grains and small inclusions in meteorites, has become more and more important in cosmochemistry [74]. The method is also utilized for U-Th-Pb dating of apatites as common accessory in igneous rocks (**Chapter 8**), based on the radioactive decay of U and Th [75],[76],[77].

3.1.7. Laser secondary neutral mass spectrometry

Laser secondary neutral mass spectroscopy (laser-SNMS) can be further divided to nonresonant laser-SNMS (NR-laser-SNMS) and resonant laser-SNMS (R-laser-SNMS). In NR-laser-SNMS (**Fig. 5(b)**), an intense laser beam is used to nonselective ionization of all atoms and molecules within the volume intersected by the laser beam. Sufficient laser power density, which is necessary to saturate the ionization process, is typically achieved in a small volume. It limits the sensitivity of the method and leads to the problems with quantification due to the differences between effective ionization volumes of different elements. Laser-SNMS method has significantly improved ionization efficiency over SIMS (a) [78],[79].

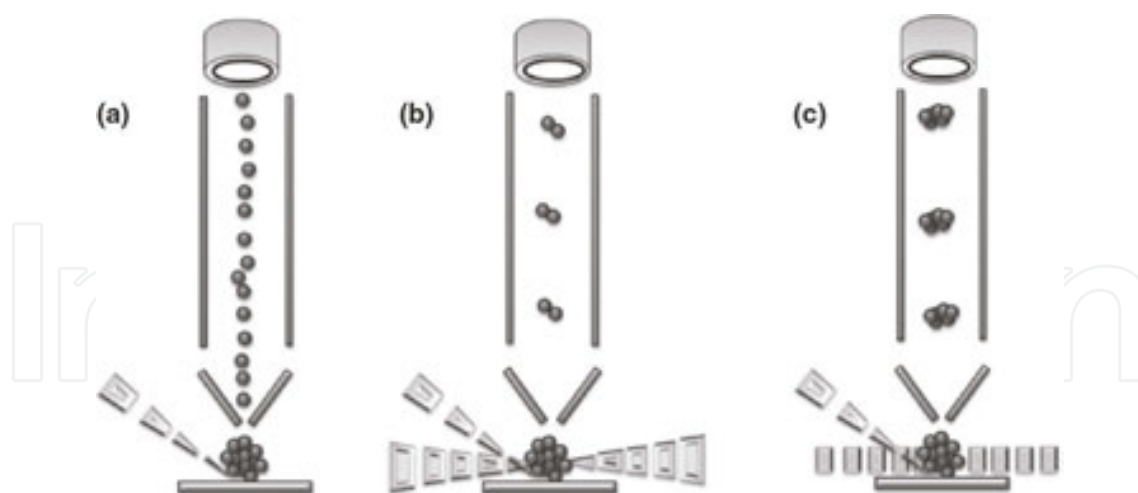


Fig. 5. Comparison of ToF-SIMS and laser-SNMS: (a) direct analysis of secondary ions (ToF-SIMS), (b) nonresonant laser-post-ionization of secondary neutrals (NR-laser-SNMS) and (c) resonant post-ionization of secondary neutrals (R-laser-SNMS) [78].

Resonant laser-SNMS uses a resonance laser ionization process, which selectively and efficiently ionizes atoms and molecules over a relatively large volume (**Fig. 5(c)**). The method has unit ionization efficiency for over 80% of elements in periodic table, i.e. the overall

efficiency is greater than that for NR-laser-SNMS, the quantification is also simpler and extremely high selectivity prevents almost all isobaric and molecular interferences [78],[79].

The method of NR-laser-SNMS was used by DAMBACH et al [80] to investigate different states of biomineralization in vitro. The results indicate that in the vicinity of single osteoblasts, extracellular enrichment of potassium typically occurs during initial stages of mineralization. Potassium may interact with matrix macromolecules and prevent an uncontrolled apatite deposition. However, apatite biomineral formation is correlated with a potassium release. In conclusion, potassium seems to be involved in the process of extracellular matrix biomineralization.

3.1.8. Electron paramagnetic resonance

The concept of electron paramagnetic resonance (EPR) spectroscopy is very similar to more familiar nuclear magnetic resonance (NMR). Both methods deal with the interaction between electromagnetic radiation and magnetic moments. In the case of EPR, the magnetic moments arise from electron rather than nuclei. The term EPR was introduced as a designation taking into account contributions from electron orbital as well as spin angular momentum. The term electron spin resonance (ESR) was also widely used because in most cases the absorption is linked primarily to the electron-spin angular momentum [82],[83]. EPR spectrum is a diagram in which the absorption of microwave frequency radiation is plotted against the magnetic field intensity [83].

The technique of electron paramagnetic resonance spectroscopy may be regarded as the consequence of the STERN–GERLACH experiment. They showed (in 1920) that an electron magnetic moment in an atom can take on only discrete orientation in a magnetic field, despite the sphericity of the atom. Subsequently, UHLENBECK and GOUDSMIT linked the electron magnetic moment with the concept of electron spin angular momentum. In hydrogen atom, there is additional angular momentum arising from the proton nucleus. BREIT and RABI described the resultant energy levels of hydrogen atom in a magnetic field. RABI et al [81] studied the transition between levels induced by an oscillating magnetic field, and this experiment was the first observation of magnetic resonance. The first observation of electron paramagnetic resonance peak was made in 1945 by ZAVOISKY, who detected the radiofrequency absorption line from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ sample using the radiofrequency (RF) source at 133 MHz [82].

The major components of EPR spectrometer are shown in **Fig. 6**. The microwave bridge supplies the microwaves at controlled frequency and power, which are transmitted to the sample cavity via the waveguide. The sample cavity is placed perpendicular to applied magnetic field, which can be varied in controlled way. In addition to this main magnetic field, a controlled but smaller oscillating magnetic field is superimposed on the cavity via the Zeeman modulation frequency. The ideal way to perform the experiment would be to apply a fixed magnetic field and vary the microwave frequency. However, microwave generators are only tunable over very limited ranges. Thus, the microwave frequency is fixed and applied magnetic field is varied. The magnetic field is applied until it reaches the value at which the sample will absorb some of the microwave energy, i.e. and EPR transition occurs [84],[85].

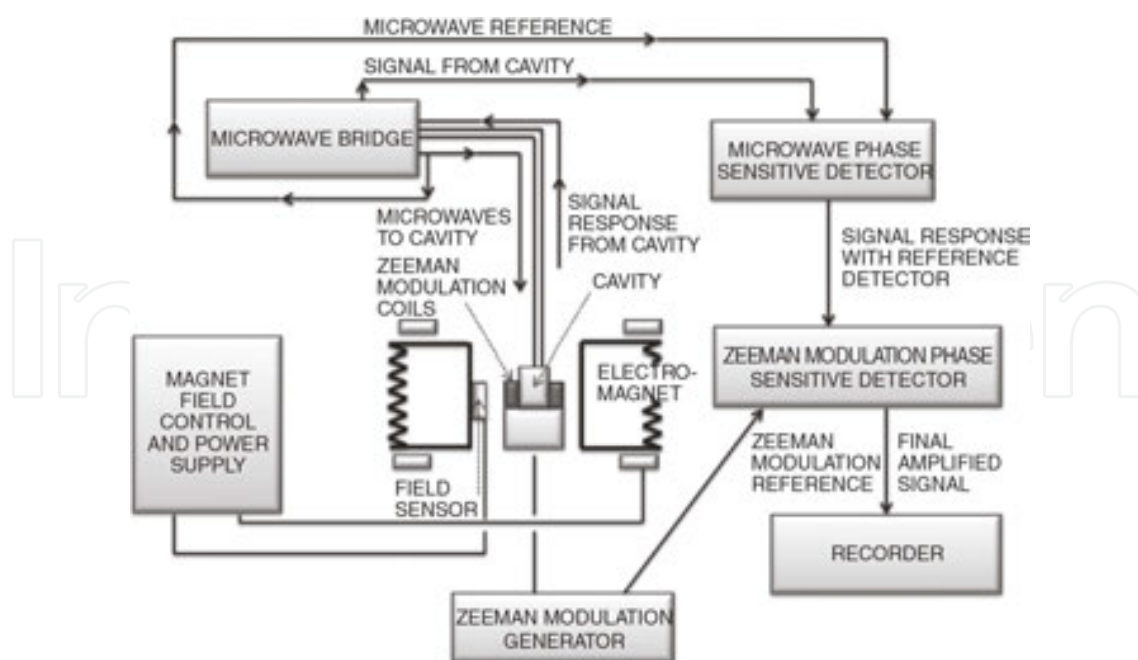


Fig. 6. The block diagram for typical continuous wave EPR spectrometer [84].

Electron paramagnetic resonance (EPR) spectrum of X-irradiated sodium and carbonate containing synthetic apatites has been studied by MOENS et al [86]. Observed spectra were decomposed in terms of five theoretical curves representing O^- radical, two CO_3^- radicals (surface and bulk) and two CO_2^- radicals (surface and bulk). These species were also described in A-type and B-type carbonate-apatites [87],[88], tooth enamel [89],[90],[91],[92], [93] and bone [94],[95], apatites, renal stones [96], etc.

3.1.9. Nuclear magnetic resonance

Solid-state nuclear magnetic resonance (NMR) is a technique for accurate measurement of nuclear magnetic moments where the resonance frequency depends on its chemical environment [97],[98],[99]. The method can provide useful information on the number of molecules in the asymmetric unit and on the site symmetry of the molecule in the lattice to assist in the refinement of powder X-ray diffraction (Section 3.1.1) data. The method can distinguish between different polymorphs. Alternatively, solid-state NMR can be used for direct and accurate measurement of internuclear distances. For amorphous and disordered solids, such as inorganic glasses and organic polymers, solid-state NMR provides structural information that cannot be obtained by any other technique [100],[101]. NMR is also the diagnostic method used in veterinary science and medicine particularly in clinical research of human brain by magnetic resonance imaging (MRI) [102].

The solution-state NMR method was developed for the investigation of structure of soluble proteins [103]. Solution and solid-state NMR are both excellent methods for the determination of chemical composition [100].

The structural information of apatites is usually investigated from ^1H , ^{19}F and ^{31}P NMR spectra of apatites [104]. The ^{31}P solid-state NMR spectroscopy is a useful tool to investigate structural information about apatites on bone organic and inorganic mineral components, as well as to investigate the crystallinity and compositional changes in carbonated apatites [105]. Intact bone is a demanding tissue for structural studies. Serious experimental problems arise from the morphological diversity of bone and from the co-existence, interrelationship and great complexity of its organic and inorganic components. Furthermore, one has to perform noninvasive analysis because bone samples are very sensitive to physical effects and chemical treatment. Solid-state ^{31}P NMR gives us a unique opportunity to look specifically at the minerals of whole bone without any chemical pretreatment, thus avoiding the intervention into the bone structure [106].

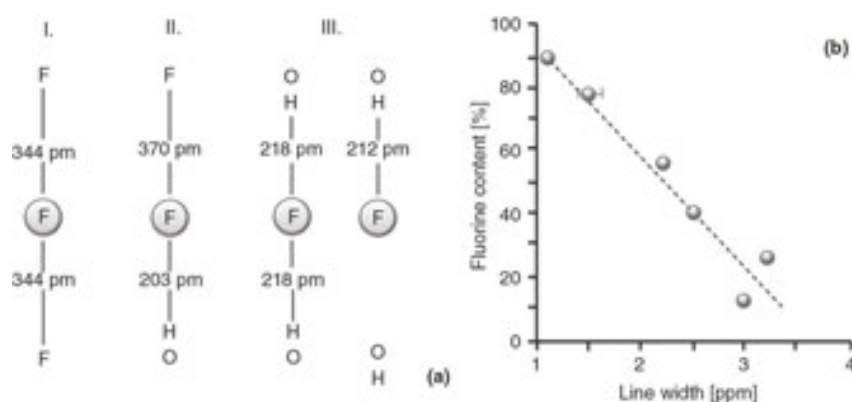


Fig. 7. Nuclear separation along parallel chains (the crystallographic c-axis) in various apatites (a): FFF group (I), FFH group (II) and HFH group (III). Correlation between observed ^{19}F line width and fluorine content of fluorinated hydroxylapatite (b) [104].

The ^{19}F NMR spectrum of fluorinated calcium hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{2x}(\text{OH})_{2-2x}$, where x is the fraction of OH^- replaced by F^-) indicates the correlation between ^{19}F chemical shift tensor parameters and the content of fluorine in apatite. The presence of OH^- groups induces perturbations of fluorine environments, involving the displacements of both fluorine and hydroxyl groups from their normal positions. This leads to a distortion of the electronic environment with regard to the investigated fluorine nucleus and gives reasons for observed change in the ^{19}F chemical shift tensor of fluoridated hydroxylapatite with different fluorine content. Furthermore, the presence of OH^- group destroys the fluoride long-range structure and that results in an isotropic chemical shift distribution. This leads to observed increase in the ^{19}F line width in the case of low fluorine content [104],[107].

3.1.10. Scanning electron microscopy, structure and elemental analysis

The scanning microscope (SEM) permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (μm) scale. In SEM, the area to be examined or the volume to be analyzed is irradiated with finely focused electron beam, which may be swept in a raster across the surface of the specimen to form an imager or

may be static to obtain the analysis at the position. The type of signals produced from the interaction of the electron beam (primary electron, PE) with the sample (**Fig. 8(a)**) includes secondary electrons (SE, with energy ≤ 50 eV), backscattered electrons (BSE, $E > 50$ eV), Auger electrons (AE), X-ray characteristics (X) and other photons of various energies such as continuum X-rays and heat. Low-loss electrons (LLE) show the energy losses of a few hundreds of eV. These signals are obtained from specific emission volumes within the sample and can be used to examine many characteristics of the sample such as surface topography, crystallography, composition, etc. [108],[109],[110].

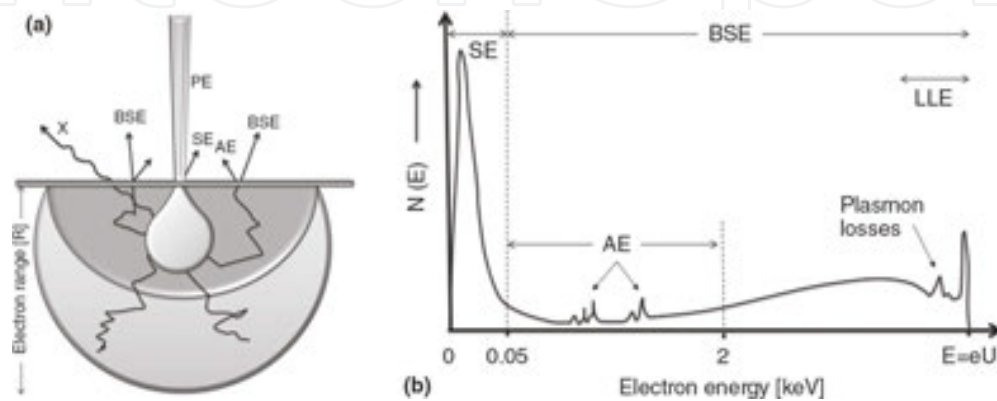


Fig. 8. Electron–specimen interaction (a) and schematic energy spectrum (a) [109].

Secondary and Auger electrons are highly susceptible to elastic and inelastic scattering and can leave the specimen only from a very thin surface layer of the thickness of a few nanometers. The most probable energy of BSE falls into the broad part of the spectrum in **Fig. 8(b)**, but they also show more or less pronounced elastic peak followed by plasmon losses, which depend on the primary energy, the take-off angle and the tilt of the specimen. Continuously slowing-down approximation assumes that the mean electron energy decreases smoothly with decreasing path length of the electron trajectories inside the specimen. The maximum information depth of BSE is of the order of half the electron range. Characteristic X-rays will only be excited in the volume in which the electron energy exceeds the ionization energy of the inner shell involved. Inelastic scattering in semiconductors results in the generation of electron-hole pairs. The recombination can take place without radiation but may result in the emission of light quanta (cathodoluminescence, CL) [111].

The method known as electron backscattering diffraction (EBDS) enables to determine the crystal structure and grain orientation of crystals on the surface of specimen. To collect maximum intensity in the diffraction pattern, the surface of specimen is stipple tilted at an angle of typically 70° from the horizontal (**Fig. 22(a)**). The intensity of backscatter **Kikuchi patterns** (please see the pattern of fluorapatite in **Fig. 23**) is rather low, as is the contrast of the signal, so extremely sensitive cameras and contrast enhancement facilities are required. This pattern allows to identify the phases and shows the misorientation across the grain boundaries [108].

Scanning electron microscope can be also used to determine compositional information using characteristic X-ray. The development of instruments for obtaining localized chemical analysis of solid samples, i.e. electron probe microanalyzer (EMPA), occurred at the same time as the development of SEM.

Scanning electron microscopy (SEM) is used for grain interactions and spot analysis [98],[112], electron microprobe microanalysis (EPMA) for the distribution of elements in the matrix, investigation of the effects of impurities on the properties of apatites and investigation of reaction interface [113],[114],[115],[116].

3.1.11. Fourier transform infrared and Raman spectroscopy

Infrared (IR) spectroscopy is one of the most important analytical techniques that can be used for the investigation of any sample in any state. Liquids, solutions, pastes, powders, films, fibers, gases and surfaces can be examined with judicious choice of sampling technique. Infrared spectrometers have been commercially available since the 1940s [117].

Fourier transform infrared (FT-IR or FTIR) spectroscopy is divided into three regions according to the increasing wavelength [118]:

1. Near-IR (NIR) spectroscopy, abbreviated as FT-NIR
2. Mid-IR (MIR) spectroscopy, abbreviated as FT-MIR
3. Far-IR (FAR) spectroscopy, abbreviated as FT-FAR

The spectral ranges of near-, mid- and far-infrared spectroscopy are shown in Fig. 9(a).

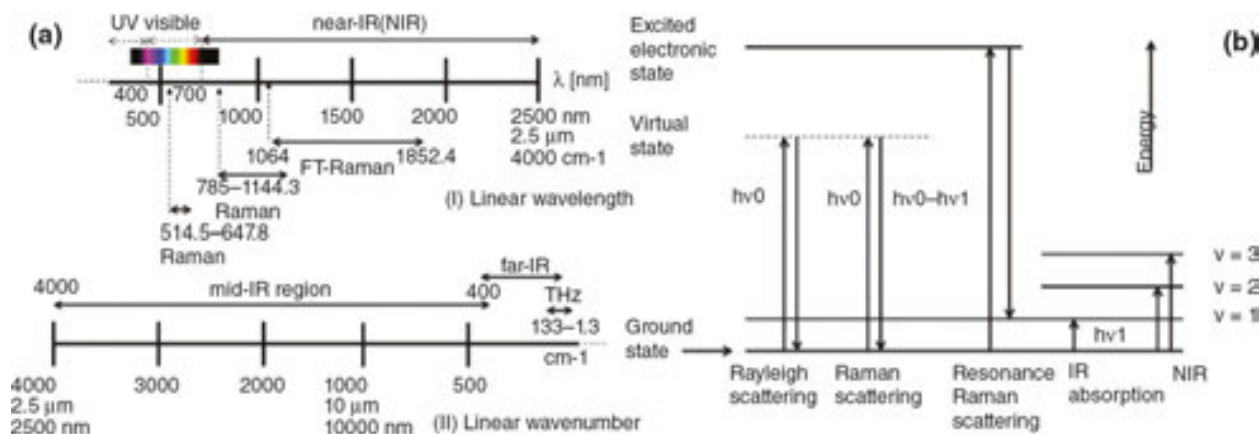


Fig. 9. Schematic illustration of relationships between the ranges of (a) vibrational spectroscopy and electromagnetic spectrum [118] and (b) spectroscopic transitions underlying several types of vibrational spectroscopy. ν_0 indicates the laser frequency, while ν is the vibrational quantum number. The virtual state is a short-lived distortion of the electron distribution by the electric field of the incident light [119].

The background for Raman spectroscopy was given by the discovery of Raman scattering by Krishna and Raman in 1928. Until approximately 1986 when Fourier transform (FT)-Raman

was introduced, physical and structural investigations dominated in literature over relatively few reports of Raman spectroscopy applied in chemical analysis [119],[120].

When monochromatic light with the energy $h\nu_0$ encounters the matter (gas, solid or liquid), there is a small probability that it will be scattered at the same frequency (**Fig. 9(b)**). If the object, e.g. molecule is much smaller than the wavelength of the light, the scattering is Rayleigh scattering. The “*virtual state*” is not necessarily a true quantum state of the molecule but can be considered a very short-lived distortion of the electron cloud caused by oscillating electric field of the light. Since blue light is more efficiently scattered than red one, Rayleigh scattering is responsible for the blue color of sky. The electron cloud of the molecule is also perturbed by molecular vibrations, and it is possible for the optical and vibration oscillations to interact, leading to Raman scattering. Raman scattering is shown in (**Fig. 9(b)**) in which the scattered photon is lower in energy by an amount equal to the vibration transition. Raman spectrum consist of scattered intensity plotted versus energy and each peak corresponds to given Raman shift from the incident light energy $h\nu_0$ [119].

Just like Rayleigh scattering, Raman scattering depends on the polarizability of scattering molecules. IR band, on the other hand, arises from a change in the dipole moment. In many cases, the transitions that are allowed in Raman are forbidden in IR, so these techniques are often complementary (please compare **Fig. 18(a)** and (**b**)). In polarizable molecules, incident light can excite the vibrational modes, leading to scattered light diminished in energy by the amount of vibrational transition energies (same as in fluorescence). Scattered light under these conditions reveals the satellite lines below the Rayleigh scattering peak at the incident frequency–Stokes lines (Stokes part of spectrum). If there is enough energy, it is also possible to see anti-Stokes lines. Since anti-Stokes lines are usually weaker than Stokes lines, only the Stokes part of spectrum is usually measured [121].

The method combining Raman spectrometer with microscopic tools, typically an optical microscope, is known as micro-Raman spectroscopy (μ RS) or also Raman microscopy. The μ RS is nondestructive and noncontact method for the characterization of organic and inorganic materials [122].

Infrared [97],[98],[123],[112],[124],[125],[126], Raman [97],[98] and micro-Raman spectroscopies [125] were often used to identify and investigate the structure and extent of substitution and to optimize the synthesis conditions of minerals from the supergroup of apatite. Since carbonate ions exhibit clear vibrational signature in infrared spectrum, infrared spectroscopy is widely used to investigate the structure and to evaluate the carbonate/phosphate ratio ($r_{c/p}$) and the amount of carbonate ions in carbonate-apatites [127]:

$$\text{CO}_3^{2-} [\text{wt.\%}] = 28.62 \, r_{c/p} + 0.0843 \quad (1)$$

The example of infrared and Raman spectrum of fluorapatite is described in **Section 3.2.3**.

Infrared spectra of phosphate minerals in the pyromorphite series are described by ADLER [128]. In the pyromorphite series, the equilibrium internuclear X-O distance in XO_4^{3-} ion (PO_4^{3-} ,

AsO_4^{3-} and VO_4^{3-}) is primarily a function of the ionic radius of X atom. Since Pb, in this case, is always the dominant externally coordinated cation, for various members, there is no significant change in the interaction between the molecular vibration and the external environment. Bradger's equation [128],[129],

$$k_0 = 1.86 \cdot 10^5 / (R - d_{ij})^3 \quad (2)$$

although specifically applicable to internuclear distances in diatomic molecules, reflects generally the inverse relationship between the force constant k_0 and the internuclear distance R . Symbol d_{ij} denotes the constant the values of which depend on the nature of bonded atoms. The molecular vibration frequency ν is dependent on the restoring forces, measured in terms of k_0 , between participating atoms as well as on the masses of these atoms. The relationship may be expressed approximately by the equation:

$$\nu = \frac{1}{2} \pi c \sqrt{\frac{k}{u}} \quad (3)$$

where the vibration frequency ν is a function of the force constant k and the reduced mass u of vibrating atoms, all other terms being invariant.

The spectral frequency differences between pyromorphite, mimetite and vanadinite are explicable and to a considerable degree predictable in terms of these parameters. On complete substitution of As or V for P the effect of reduced force constants is reinforced by increases in mass, thereby shifting ν_3 and ν_1 to lower frequencies. Because of opposing mass and force-constant effects and perhaps also because of dissimilarities in orbital configurations, the relative positions of absorption bands are less predictable for mimetite and vanadinite than for pyromorphite and mimetite. The theoretical frequency trends are depicted in Fig. 10 [128].

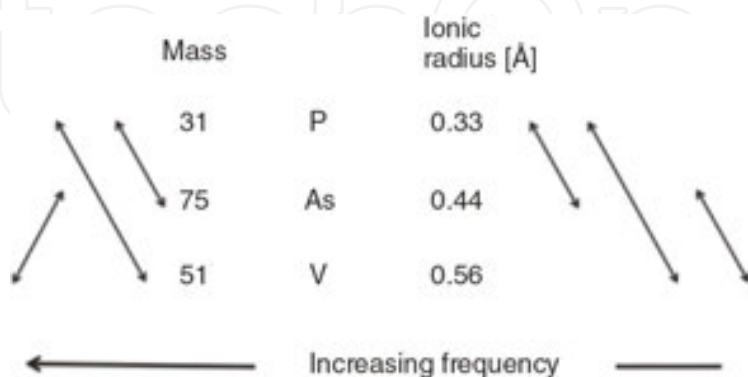


Fig. 10. Theoretical effect of change in mass and ionic radius on infrared vibration frequency of tetrahedral XO_4^{3-} ions, where $\text{X} = \text{P}^{5+}$, As^{5+} or V^{5+} [128].

3.1.12. Thermal analysis

Thermal analysis (TA) refers to a group of techniques¹⁰ in which the property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere¹¹ is programmed. These methods study the relationship between sample property and its temperature as the sample is heated or cooled in a controlled manner. The individual techniques are divided according to the measured property¹² [131],[132], [130] as is introduced in **Table 1**.

Property	Technique and abbreviation		Notes
Heat	Scanning calorimetry	–	–
Temperature	Thermometry	–	Also can be described as heating or cooling curve
Temperature difference	Differential thermal analysis	DTA	A technique where the temperature difference between the sample and reference material is measured
Heat flow rate difference	Differential scanning calorimetry	DSC	A technique where the difference between heat flow rates into the sample and reference material is measured
Mass	Thermogravimetry or thermogravimetric analysis	TG or TGA	The abbreviation TG has been used, but should be avoided, so that it was not confused with T_g (temperature of glass transition)
Dimensional and mechanical properties	Dynamic mechanical analysis	DMA	Moduli (storage/loss) are determined
	Thermomechanical analysis	TMA	Deformations are measured
	Thermodilatometry	TD	Dimensions are measured
Electrical properties	Dielectric thermal analysis	DEA	Dielectric constant/dielectric loss are measured
	Thermally stimulated current	TSC	Current is measured
Magnetic properties	Thermomagnetometry	TM	Often combined with TGA
Gas flow	Evolved gas analysis	EGA	The composition and/or the amount of gas/vapor is determined
	Emanation thermal analysis	ETA	Trapped radioactive gas within the sample is released and measured
Pressure	Thermomanometry	–	Evolution of gas is detected by pressure change

¹⁰ The definition of terms in thermal analysis was developed by ICTAC (Confederation for Thermal Analysis and Calorimetry).

¹¹ Gaseous environment of the sample, which may be controlled by the instrumentation or generated by the sample [130].

¹² Resulting dependence, i.e. any graph of any combination of property vs. time or temperature derived from a thermal analysis technique, should be termed as thermal curve, which is a simplified form of more correct term thermoanalytical curve. The first mathematical derivation of any curve with respect to temperature or time leads to the derivative thermoanalytical curve [130]. Since the name thermogram has medical usage, the thermal analysis curve should not be termed as thermogram [131].

Property	Technique and abbreviation		Notes
Optical properties	Thermobarometry	–	Pressure exerted by dense sample on the walls of a constant volume cell is studied
	Thermooptometry or thermooptical analysis	TOA	A family of techniques in which optical characteristics or property of the sample is studied
Acoustic properties	Thermoluminescence	TL	Light emitted by the sample is measured
	Thermosonimetry or thermoacoustimetry	TS	Emitted (sonimetry) or absorbed (acoustimetry) sound is measured.
Structure	Thermodiffractometry	–	Techniques where the compositional or chemical nature of the sample is studied.
	Thermospectrometry		

Table 1 Methods of thermal analysis according to measured property or physical quantity.

The measurement should be performed as follows:

1. **Combined:** the application of two or more techniques to different samples at the same time. This can include thermal and nonthermal analytical techniques.
2. **Simultaneous:** indicates the measurement of two or more properties of a single sample at the same time.

The sample-controlled method where the feedback used to control the heating is the rate of transformation is termed as controlled-rate thermal analysis (CRTA) [130].

Simultaneous thermogravimetry (thermogravimetric analysis) and differential thermal analysis (TG-DTA) are mostly used to investigate the course of synthesis and the characterization of prepared apatites or to investigate the process of thermal decomposition of apatites, i.e. the processes such as dehydroxylation (e.g. **Section 1.5.2**), defluorination (**Section 3.2.4** and **8.6**), decarbonation (thermal decomposition of carbonate-apatites, **Section 4.6.1**), etc.

3.1.13. Optical properties

The analysis of optical properties is essential for each mineral examined, and through the use of microscopy, the optical properties of individual minerals may be interpreted in great detail. Optical mineralogy investigates the interaction of light (usually is limited to visible light) with minerals and rocks. Optical mineralogy concerns mainly the use of polarizing (petrographic) microscope which has two Nicol prisms, polarizer and analyzer (polarizer below the stage and the analyzer above the objective) [133]. Human eye is the most sensitive for viewing a solid in the wavelength symmetrically spread in intensity around 550 nm (**Fig. 11(a)**). Optical microscopy in visible light (from 700 nm (red) to 420 nm (violet), **Fig. 11(b,c)**) helps study the objects of smaller sizes up to lower limit of ~ 1 μm (c). **Fig. 11(d)** shows the scope of spectroscopic techniques associated with electromagnetic spectrum [134].

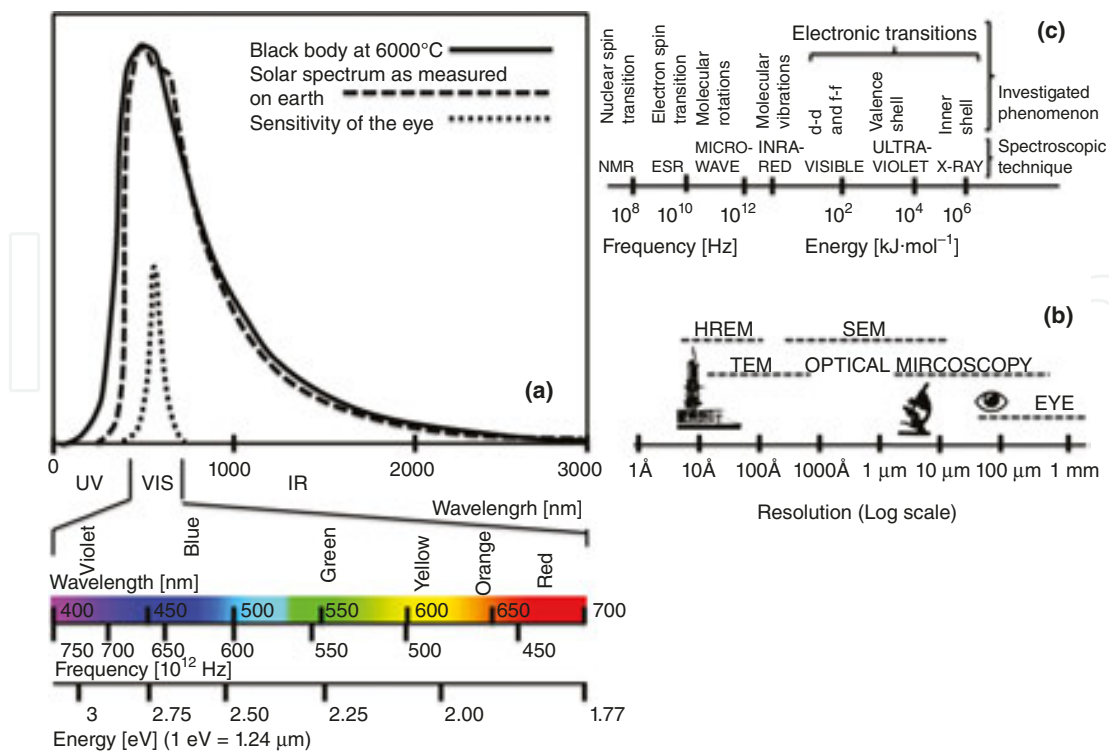


Fig. 11. Electromagnetic spectrum of solar radiation and black body (a), the resolution of various techniques (b) and the regions associated with spectroscopic techniques (c) [134].

Refractive index (n) is related to the angle of incidence (i) and the angle of refraction (r) according to the Snell's law:

$$n = \sin i / \sin r \quad (4)$$

The refractive index increases as the wavelength of light decreases [134]. The absorption coefficient is related to the imaginary part of the refractive index. It was found that since the refractive index of a medium depends on the density of electrons in that medium, the index increases with the density of matter [135].

The luster of mineral (R) depends of the way in which the light is reflected from the surface of a mineral. The reflection is again dependent on the refractive index. Normally, the greater is the index of refraction, the brighter is the luster. The luster is classified into two broad classes [134]:

- Nonmetallic luster: results from the interaction of light with dielectric semiconducting and poorly conducting substances
- Metallic luster: occurs in minerals having metallic bonding (e.g. native metals) or high degree of covalent bonding (sulfides, sulfosalts, etc.)

Optical properties of apatites can be determined using the complex dielectric function [136], [137], [138]

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (5)$$

in the range of linear response. By calculating the wave function matrix and using Kramers–Krönig relations, the imaginary and real part of the dielectric function $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ can be derived respectively as follows:

$$\varepsilon_2(\hbar\omega) = \frac{e^2}{\pi m \omega^2} \int_{BZ} dk^3 \sum_{n,l} \left| \langle \Psi_n(\bar{k}, \bar{r}) | \right\rangle - i\hbar \left| \langle \Psi_l(\bar{k}, \bar{r}) | \right\rangle^2 f_1(\bar{k}) \quad (6)$$

$$\left[1 - f_n(\bar{k}) \right] \delta \left[E_n(\bar{k}) - E_l(\bar{k}) - \hbar\omega \right]$$

where $f(k)$ is the Fermi distribution function, l and n mark occupied state and unoccupied state, respectively. $\Psi_n(k, r)$ is the Bloch wave function for the n th band with the energy $E_n(k)$ at the Brillouin zone point k . The matrix element momentum transition corresponds to the term $|\langle \Psi_n(\bar{k}, \bar{r}) | - i\hbar | \langle \Psi_l(\bar{k}, \bar{r}) |^2$.

For each apatite, the real part ε_1 and imaginary part ε_2 of dielectric function have similar features with some subtle differences. The real part ε_1 has two main peaks:

1. First peak lies near the energy of 7 eV. Obviously, the first peak is caused by the transitions from O-2p and P-3p levels.
2. The second peak lying at ~25 eV results from the transitions from Ca-3p levels.

The ε_2 curve in the energy range from 5 to 15 eV characterizes three main peaks:

1. The first peak lies in 7.10, 7.16 and 7.43 eV for FAP, ClAP and BrAP, respectively.
2. The second peak is located at 8.51, 8.62 and 8.76 eV for FAP, ClAP and BrAP, respectively.
3. The third peak is situated at 10.99, 11.08 and 11.45 eV for FAP, ClAP and BrAP, respectively.

The refractive index n can be obtained by $n = \sqrt{\varepsilon_1(0)}$. The $\varepsilon_1(0)$ for FAP, ClAP and BrAP are 1.38, 1.41 and 1.46, respectively. Therefore, the refractive indexes for FAP, ClAP and BrAP are 1.17, 1.19 and 1.21. Moreover, analogous dielectric function curves and similar refractive index values show that the optical property of each apatite has some independence from the c -axis ion [136].

3.1.14. Measuring of surface area, porosity and pore size distribution

There is a conventional mathematical idealization that asserts that a cube of edge length a possesses a surface area of $6a^2$ and that a sphere of radius r exhibits $4\pi r^2$. In reality, however, mathematical perfect or ideal geometric forms are unattainable (Fig. 12) since all real surfaces exhibit flaws under microscopic examination. Real surface irregularities (voids, pores, steps, etc.) make the real surface area greater than corresponding theoretical area. When the

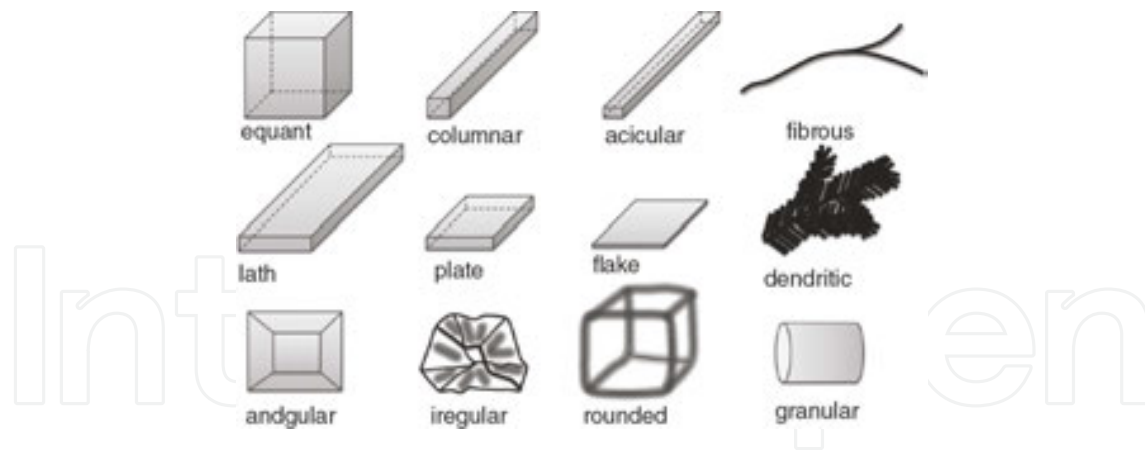


Fig. 12. Description of particle shapes [140].

cube, real or imaginary, of one meter edge length is subdivided into smaller cubes each one micrometer (10^{-6} m) in length, there will be 10^{18} particles formed, each exposing an area of 6×10^{-12} m². Thus, the total area of all particles is 6×10^6 m². This operation increases by million-fold the exposed area of fine powder compared to undivided material. Whenever the matter is divided into smaller particles, new surfaces must be produced with corresponding increase in surface area [139],[140].

The particle size distribution (PSD) was usually determined by sieve analysis, sedimentation methods (gravitational or centrifugal), microscopic techniques, light scattering, multiangle laser light scattering (MALLS), etc. [141].

The range of specific surface area, i.e. area per gram of matter, can vary widely depending on the particles' size, shape and porosity. The influence of pores can often overwhelm the size and external shape factors. The powder consisting of spherical particles exhibits total surface (S_t) and volume ($V = M/\rho$) [139]:

$$S_t = 4\pi (r_1^2 N_1 + r_2^2 N_2 + \dots + r_n^2 N_n) = 4\pi \sum_{i=1}^n r_i^2 N_i \quad (7)$$

$$V = \frac{4}{3}\pi (r_1^3 N_1 + r_2^3 N_2 + \dots + r_n^3 N_n) = \frac{4}{3}\pi \sum_{i=1}^n r_i^3 N_i \quad (8)$$

$$S = \frac{S_t}{M} = \frac{3 \sum_{i=1}^n N_i r_i^2}{\rho \sum_{i=1}^n N_i r_i^3} \quad (9)$$

where r_i and N_i are the average radii and numbers of particles in the fraction i . For spheres of uniform size, Eq. 9 becomes the law:

$$S = \frac{3}{\rho r} \quad (10)$$

Besides the calculation of specific surface from its geometry and PSD curve, the adsorption isotherm (predominantly Langmuir and BET¹³), air permeability methods,¹⁴ and monolayer sorption methods were used to determine the specific surface area [142],[143].

The porosity is defined as the ration of pore volume to total volume. Porous material is defined as solids containing pores **Fig. 13(a)**, which are classified into two major types: open and closed pores. Penetrating open pores (interconnected pores) are permeable for fluid and therefore are important in applications such as filters. Pores accessible from only one end are referred to as dead-end pores. Noninterconnected (closed) pores are not accessible at all. The classification of pores according to their size is shown in **Fig. 13(b)**. Pores can be also classified as the pores among agglomerates and pores among primary particles (**Fig. 13(c)**) [144],[145].

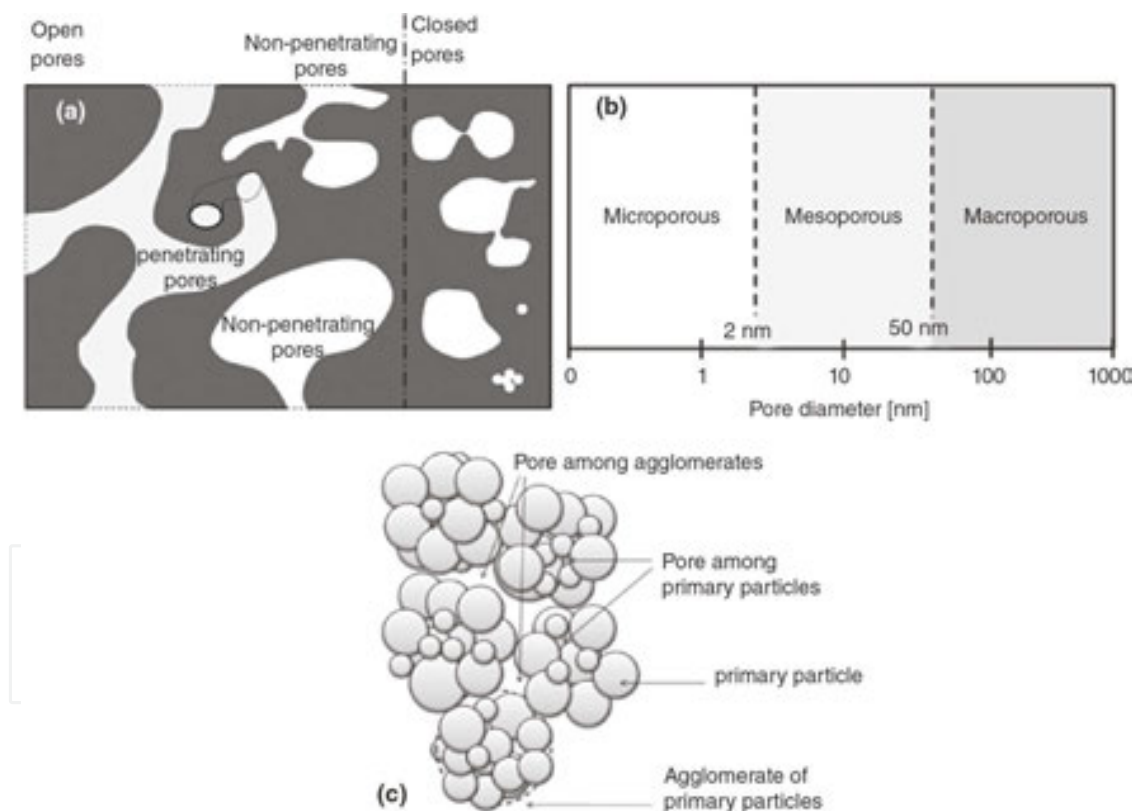


Fig. 13. Schematic illustration of different morphology of pores (a) and classification of porous materials based on pore size (b) and schematic illustration of pores among agglomerates and primary particles (c) [144].

¹³BRUNAUER-EMMETT-TELLER (BET) theory of multilayered physical adsorption of gas molecules on a solid surface [143].

¹⁴ For example, the Blaine method, where fixed volume of air passes through the bed at steadily decreasing rate, which is controlled and measured by the movement of oil in a manometer, the time required being measured. The method is widely used for the determination of specific surface area of cements [143].

Pore size distribution and permeability¹⁵ are a very desirable quantities for the characterization of structure of porous solids, which can be determined by the following [145],[146],[147]:

- i. Stationary fluid (static) method
- ii. Capillary pressure (HASSLER¹⁶) method
- iii. Quasi-steady-state methods, including the gas drive method and the solution-gas drive method.

The surface area and the porosity of apatites have effect on the floatability (**Section 8.7**) of apatites of different type and origin [148]. The surface area, the porosity and the pore size distribution are properties of great importance for the preparation of biological apatites in tissue engineering (**Section 10.9**) and tailoring their mechanical properties, solubility and bioactivity [149],[150],[151],[152]. Ionic surfactants, such as decyltrimethylammonium bromide ($\text{CH}_3(\text{CH}_2)_9\text{N}(\text{CH}_3)_3(\text{Br})$, C(10)TAB), hexadecyltrimethylammonium bromide ($\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$, C(16)TAB), as well as nonionic surfactant, can be used to control the pore (pore size and volume) and surface characteristics of mesoporous apatite materials under maintained pH [153]. The porosity also affects electrical properties of oxyapatites (**Chapter 5**) [154],[155],[156].

3.2. Investigation and characterization of apatite specimen

3.2.1. Identification of the specimen

Some techniques mentioned above will be demonstrated on the specimen of apatite sample (**Fig. 14(a)**) from Sljudjanka, Bajkal. The translucent specimen with glassy luster is greenish blue colored and brittle as can be seen from large amount of smoothly curving conchoidal fractures on the surface (please see also **Fig. 20**). When scratched by a single crystal of corundum (**Fig. 14(b)**), the sample shows white colored scratch. Since the sample surface can be also scratched by feldspar (**Fig. 14(c)**) but not by fluorite, the hardness in the Mohs scale¹⁷ is equal to 5, i.e. corresponds to apatite.

¹⁵ The flow of fluids through porous materials is of great importance in the fields of industrial chemistry, oil technology, and agriculture. In general, it may be stated that the principal interest is in the transport through reactive materials [147].

¹⁶ Experimental techniques for the measurement of relative permeability can be divided to steady- (1) and unsteady-state (displacement) methods (2). The steady-state method was developed by HASSLER (1944). Semipermeable membranes are provided at each end which keeps the fluids separated, except inside the core where the fluids flow simultaneously. The pressure is measured in each phase through semipermeable barriers, and the pressure differences between the phases are maintained constant throughout the medium so as to eliminate the capillary end effect as well as to ensure a uniform saturation along the core. The saturation can be altered by applying capillary pressures across the nonwetting phase ports and wetting phase semipermeable membranes [146].

¹⁷ The Mohs scale of mineral hardness is graduated as follows: talc (1), gypsum (2), calcite (3), fluorite (4), apatite (5), orthoclase (6), quartz (7), topaz (8), corundum (9), and diamond (10). Apatite should be also scratched by steel knife (up to 5.5) and glass (up to 6).



Fig. 14. Specimen of apatite from Sljudjanka, Bajkal (a) shows white color of scratch (b). The sample can be also scratched by minerals with hardness ≥ 6 (feldspar and higher) on the Mohs scale (c).

The microhardness of apatite sample was then determined by Vickers microhardness test.¹⁸

Fig. 15 shows the replica of diamond pyramid base¹⁹ on the surface after the indentation of sample. The average hardness of sample was determined to be 552 (± 30) HV 0.05/10. The formation of radial cracks on the corners indicates brittle material [157]. According to the mineral hardness conversion charts, the measured value is in good agreement with the tabular value of apatite (535 HV [158]).

Moreover, the sample does not show any luminescence when elucidated by long UV light (**Fig. 16(a)**). The specific gravity of the specimen was assessed by hydrostatic weighting (b) and pycnometric technique (c) to be 3.18 and $3.16 \pm 0.20 \text{ g}\cdot\text{cm}^{-3}$, respectively. These values are in a good agreement with average density of apatite ($3.19 \text{ g}\cdot\text{cm}^{-3}$, **Chapter 1**). All properties of investigated specimen mentioned above identify it as apatite, but the exact kind of apatite mineral and its chemical composition must still be determined yet.

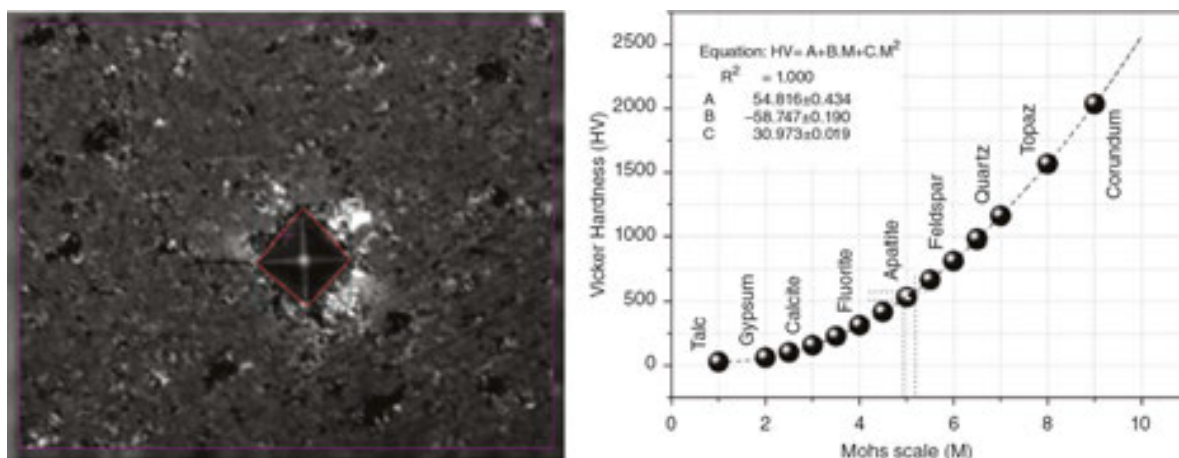


Fig. 15. The Vickers microhardness test with the load of 0.05 kgf for the time of 10 s and the correlation of results with the Mohs scale.

¹⁸ Hardness tester LECO AMH 43. The method is also known as the Vickers pyramid number (HV) or the diamond pyramid hardness (DPH).

¹⁹ Diamond pyramid with apical angle of 136° .



Fig. 16. The specimen of apatite under UV light (compared with the fragment of red luminescence of alumina).

The sample was next treated to fine powder via milling in stain-less steel laboratory vibration mill. The apatite mineral was then determined by X-ray diffraction analysis (**Fig. 17**), mid-infrared spectroscopy (**Fig. 18**) and EBSD (**Fig. 23**) as fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$, ref. [159]) with small amount (1%) of accessory mineral calcite²⁰ (CaCO_3). Since the crystallographic parameters of identified hexagonal apatite are $a = 9.3917$, $c = 6.8826 \text{ \AA}$ and $Z = 2$, it is possible to calculate the axial ratio (**Eq. 11**), the volume of cell (**Eq. 12**) and the density (**Eq. 13**) as follows:

$$a:c = 1:0.7328 \quad (11)$$

$$V = a^2 c \sin(60) = 9.3917^2 6.8826 \sin(60) = 525.74 \text{ \AA}^3 \quad (12)$$

$$\begin{aligned} \rho_{\text{calculated}} &= \frac{M_{\text{apatite}} Z}{V \frac{N_A}{1 \times 10^{24}}} = \frac{504.31 \times 2}{525.74 \frac{6.025 \times 10^{23}}{1 \cdot 10^{24}}} \\ &= 3.19 \text{ g} \cdot \text{cm}^3 \end{aligned} \quad (13)$$

where M is the molecular weight of fluorapatite (**Table 7 in Chapter 1**) and N_A is the Avogadro constant. The reconstruction of the cell of investigated apatite specimen is shown in **Fig. 24**.

3.2.2. X-ray diffraction analysis

Powder X-ray diffraction analysis of the apatite specimen (**Fig. 17**) identified it as fluorapatite. According to quantitative Rietveld analysis, the sample contains 99% of fluorapatite. There is also small amount (1%) of calcite²¹ that occurs on the surface of apatite specimen. Since the fluorapatite specimen (**Fig. 14**) is single crystal (**Section 3.2.6**), the crystal faces cannot be recognized, i.e. the crystal habit is anhedral (refer to **Footnote 2 in Chapter 2**). Nevertheless, XRD pattern shows that the most intensive diffraction possesses the Miller index (211), which corresponds to the Miller-Bravais indices (21–31), i.e. dihexagonal dipyramid (**Chapter 1**).

²⁰ Since it is present as “free carbonate,” the sample cannot be considered as carbonate-fluorapatite (**Section 2.6 and 4.6.1**).

²¹ As the results of thermal analysis revealed (**Section 3.2.4**), the Rietveld analysis slightly overestimates the content of free carbonate in the sample.

There is also basal pinacoid {1000}, first-order {10–10} and second-order {11–20} hexagonal prism and dihexagonal prism {21–30}.

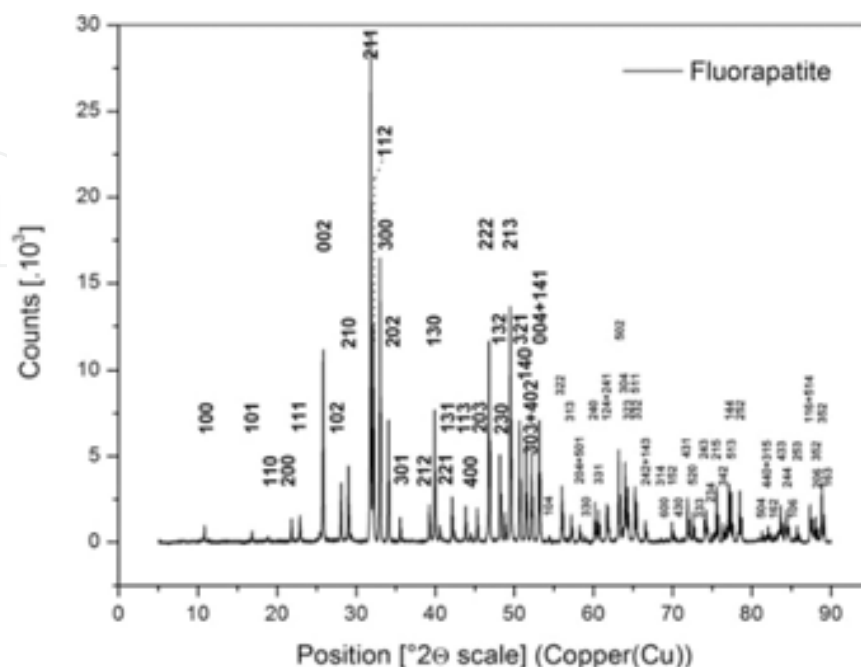


Fig. 17. X-ray diffraction analysis of investigated specimen of apatite.

It is obvious that fluorapatite belongs to the hexagonal-dipyramidal crystal system, but the estimation of crystal habit of corresponding euhedral crystals from these results is highly speculative due to possible combination of pinacoid (*c*), first-order (*m*) and second-order hexagonal prisms (*a*) and first-order (*p*) and second-order dipyramids (*s*) with dihexagonal dipyramid (*v*) faces in the single crystal.

3.2.3. Infrared and Raman spectroscopy

Infrared (mid-FT-IR²²) and Raman spectrum of fluorapatite is shown in **Fig. 18(a)** and **(b)**, respectively. The most expressive infrared bands are attributed to fundamental frequencies of tetrahedral phosphate ion $[\text{PO}_4]^{3-}$. The structure of apatite leads to the reduction of ion symmetry from T_d (four fundamental frequencies with IR inactive ν_1 mode) to C_{2v} , where ν_1 mode becomes IR active [128],[160],[161],[162],[163]:

1. The $\nu_1(\text{PO}_4)$ mode is very weak (*vw*²³) band that is related to symmetric stretching of phosphate ion.
2. Bending: ν_2 mode (*vw*).

²² Baseline corrected spectrum measured by KBr technique.

²³ Abbreviation used for the expression of intensity and width of peak in the spectrum: very weak (*vw*), weak (*w*), middle (*m*), strong (*s*) and very strong (*vs*), shoulder (*sh*), broad (*b*), very broad (*vb*), and sharp (*sp*). Spectral bands related to impurities are abbreviated as *imp* [162].

- 3. Anti-symmetric stretching: ν_3 mode is the strongest (vs , vb) band in the infrared spectrum appearing in the spectral region from 1000 to 1150 cm^{-1} .
- 4. Bending: ν_4 mode (m , vb) is observed between 540 and 620 cm^{-1} .

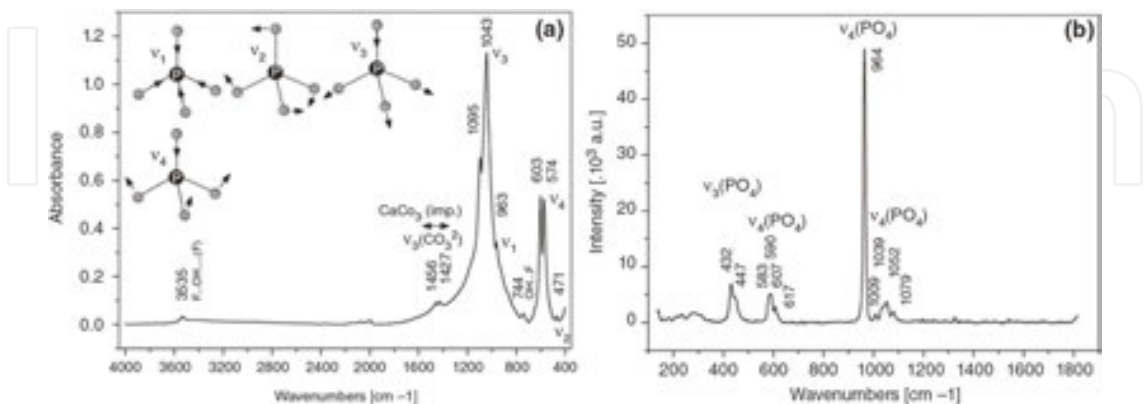


Fig. 18. Infrared (a) and Raman (b) spectrum of investigated specimen of fluorapatite.

The crystallinity of natural and synthetic apatite samples is often determined from the broadening of $\nu_4(\text{PO}_4)$ infrared absorption bands [160]. The assignment of bands in infrared and Raman spectrum of fluorapatite is listed in **Table 2**.

Vibration mode	Assignment C_{6h} factor group symmetry	Raman shift [cm^{-1}]	IR
ν_1	A_g, E_{2g}, E_{1u}	956	965
ν_2	E_{1g}	432	—
	E_{2g}	—	—
	A_g	449	—
	E_{1u}	—	460
	A_u	—	470
ν_3	A_u, E_{2g}	1034	1032
	E_{1g}, E_{1u}	1042	1040
	A_g	1053	—
	E_{2g}	1061	—
	A_g	1081	—
	E_{1u}	—	1090
ν_4	A_u	—	560
	E_{1u}	—	575
	E_{2g}	581	—

Vibration mode	Assignment C _{6h} factor group symmetry	Raman shift [cm ⁻¹]	IR
	A _g , E _{1g}	592	–
	E _{1u}	–	601
	A _g	608	–
	E _{2g}	617	–

Table 2. The interpretation of infrared and Raman bands in the spectrum of stoichiometric fluorapatite [164].

Factor group analysis of the hexagonal P6₃/M space group fluorapatite structure (Z = 2) yields an irreducible representation for optically active vibration of [165]:

$$\Gamma = 12 A_g(R) + 7 A_u(IR) + 8 E_{1g}(R) + 11 E_{1u}(IR) + 13 E_{2g}(R) \tag{14}$$

where IR and R denote infrared and Raman activity, respectively. The influence of pressure on the infrared and Raman spectra of fluorapatite was investigated by WILLIAMS and KNITTLE [165]. Fluorapatite remains stable under pressures of at least 25 GPa at 300 K. Local environment of phosphate groups in fluorapatite becomes progressively less distorted from tetrahedral symmetry under the compression, as manifested by progressively smaller site-group.

The Davydov (factor group) splitting also decreases under the compression. This decrease is consistent with nondipole effects playing a primary role in the Davydov splitting of apatite; indeed, the magnitude of the Davydov splitting appears to be modulated by increases of the site symmetry of phosphate group under the compression [165].

The spectrum **Fig. 18(a)** shows weak peak located in the domain of OH stretching modes (from 3500 to 3600 cm⁻¹) at the wave number of 3535 cm⁻¹. This band belongs to the OH stretching mode in the hydrogen bond F...OH...(F) [166]. According to FREUND and KNOBEL [167], the band at ~744 cm⁻¹ belongs to the vibration of OH...F bond. According to KNUBOVETS [168], the bands in the range from 745 to 720 cm⁻¹ in apatite spectra could also be attributed to symmetric valence oscillations of the P-O-P bridge bonds, formed by the condensation of the PO₄³⁻ tetrahedron. The presence of calcite causes that antisymmetric stretching mode (ν₃) of planar CO₃²⁻ ion appears in the infrared spectrum of investigated sample [169].

3.2.4. Thermal analysis

The results of simultaneous TG-DTA of investigated fluorapatite specimen are shown in **Fig. 19**. The sample is heated with the rate of 10°C·min⁻¹ up to the temperature of 1425°C. The mass of sample is reduced by 1.25% during TG-DTA when the final temperature is reached. The most important features are the thermal decomposition of CaCO₃ and the thermal decomposition of fluorapatite.

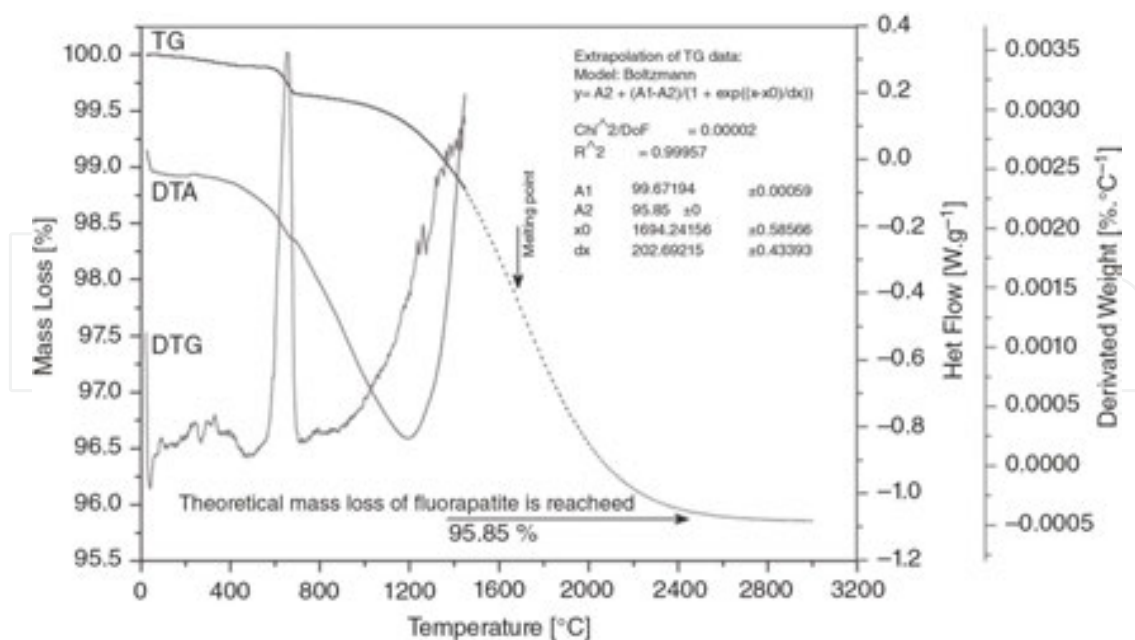


Fig. 19. Thermal analysis of investigated specimen of fluorapatite.

The content of calcite was verified by thermal analysis. The weight of sample was reduced by 0.26% during the thermal decomposition of calcite. Since the theoretical mass loss of calcite is $(100 \times 44.09) / 100.086 = 43.97\%$,²⁴ the content of calcite in the investigated sample of fluorapatite is $(100 \times 0.26) / 43.97 = 0.59\%$. Although this value is lower than the content of calcite determined by Rietveld analysis, there is still good agreement of both methods. The DTG curve shows that the process starts at the temperature of 565°C and wide of peak is of 135°C. The maximum rate decarbonation is reached at the temperature of 656°C.

At temperatures higher than 900°C, the weight of sample is reduced by the thermal decomposition of fluorapatite. The extrapolated beginning of the defluorination process (**Section 8.6**) was determined to be 1199°C. At the temperature of 1425°C, the defluorination process is still not complete. The extrapolation of experimental data²⁵ shows that the thermal decomposition is most probably not complete before the temperature of melting point is reached (**Table 7 in Chapter 1**).

3.2.5. Scanning electron microscopy and WDX analysis

The microphotographs from SEM analysis of break plane of investigated fluorapatite specimen are shown in **Fig. 20**. The series of conchoidal fractures on the surface show brittle fracture as further characteristic properties of apatite.

²⁴ It was calculated as $100 \times \text{molar mass (molar weight) of } CO_2 / \text{molar mass of } CaCO_3$.

²⁵ Theoretical mass loss (3.77%) of fluorapatite was used to set the fixed value of parameter A_2 .

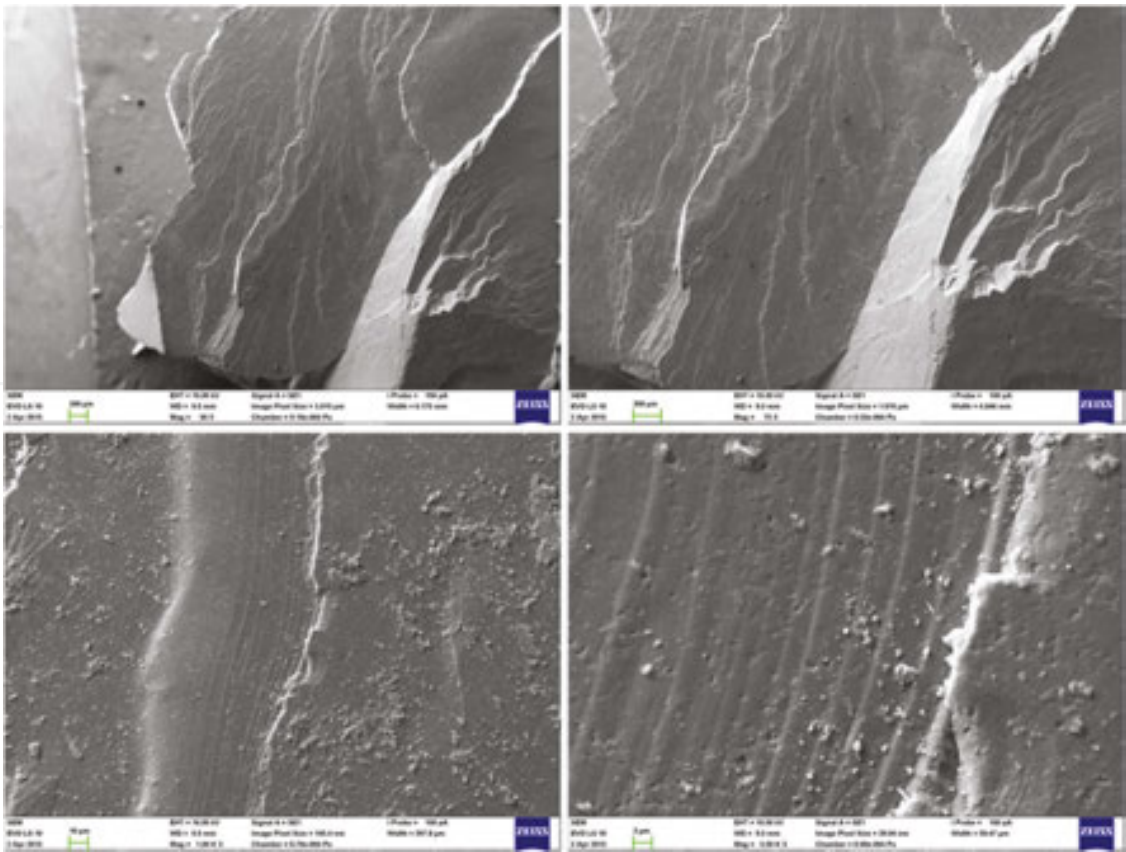


Fig. 20. SEM image of the break plane of investigated fluorapatite specimen: 50× (a), 75× (b), 1 000× (c) and 5 000× (d).

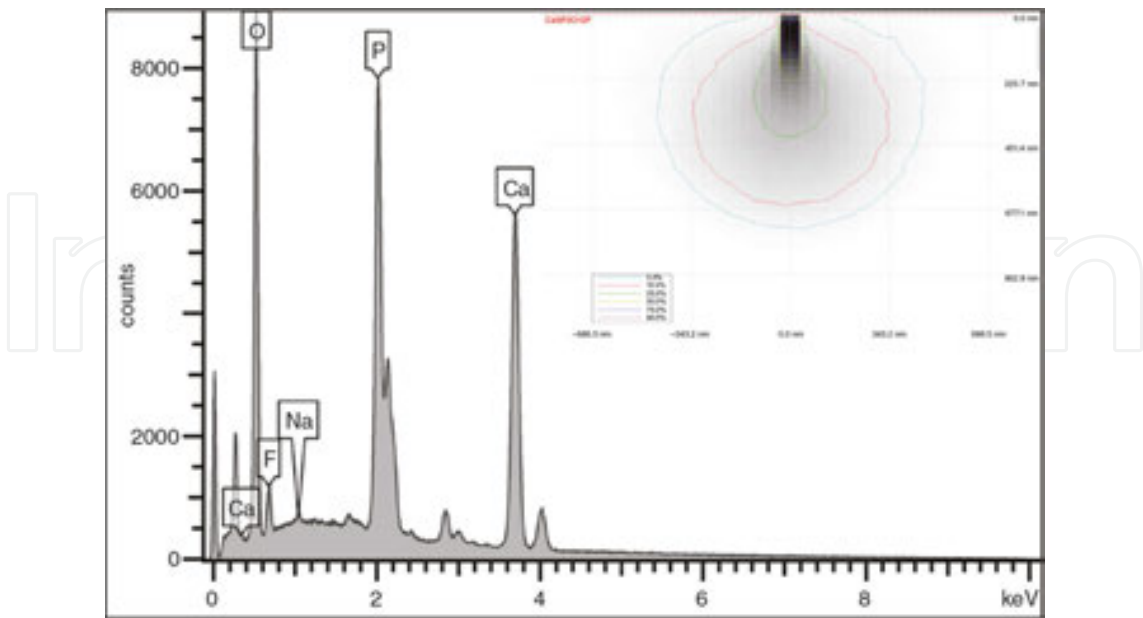


Fig. 21. Typical results of WDX analysis of the fluorapatite specimen and simulation of electron–specimen interaction.

The chemical composition of sample was determined by WDX analysis (**Fig. 21**). The average results are introduced in **Table 3**.

Element	Ca	P	O	F	Na
Weight [%]	38.64 ± 0.96	16.86 ± 0.47	40.55 ± 1.37	3.75 ± 0.08	0.23 ± 0.03
Ideal composition*	39.74	18.43	38.07	3.77	–
Atomic [%]	22.67 ± 0.85	12.81 ± 0.52	59.63 ± 1.31	4.65 ± 0.05	0.24 ± 0.03
Atomic ratio	4.91 ± 0.31	2.78 ± 0.18	12.77 ± 0.19	1	0.05 ± 0.01
Ideal composition ²⁶	5	3	12	1	–

Table 3. Average chemical composition of investigated specimen of fluorapatite.

The composition of fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F} \rightarrow \text{Ca}_5\text{P}_3\text{O}_{12}\text{F}$) corresponds to the element ratio: Ca:P:O:F = 5:3:12:1. The results of WDX analysis of investigated specimen (**Table 3**) are in good agreement with the composition of ideal fluorapatite and fulfill all the criteria mentioned in **Section 1.4**.

3.2.6. EBDS analysis

The fragments of investigated fluorapatite specimens (**Fig. 22**) were further investigated by EBDS analysis.



Fig. 22. Sample stage (a) and microphotograph of fluorapatite fragments used for EBDS (b).

The Kikuchi patterns confirm the sample as single crystal of fluorapatite **Fig. 23**.

²⁶. Resulting from the apatite formula (**Section 1.4**).

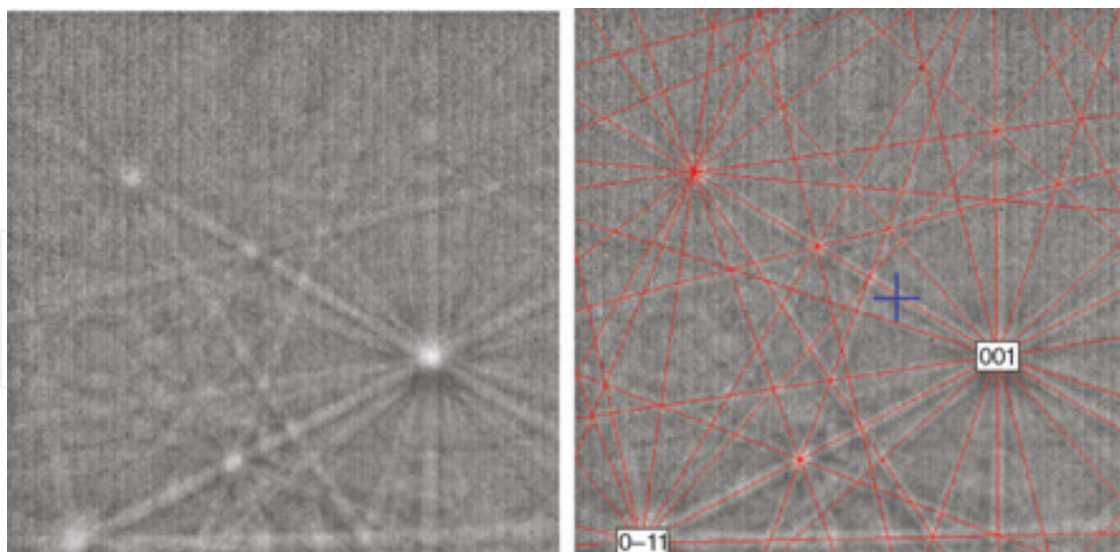


Fig. 23. EBSD analysis of investigated fluorapatite specimen.

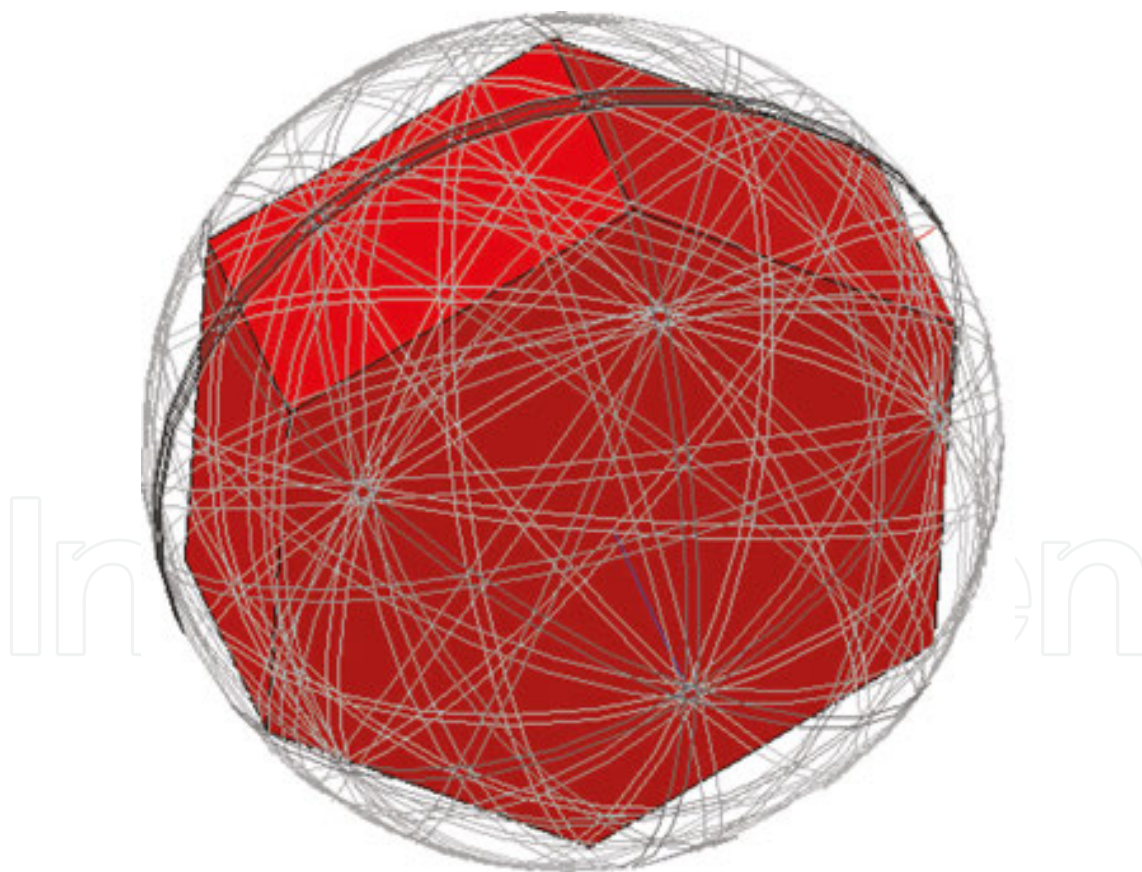


Fig. 24. The Kikuchi sphere showing the orientation of apatite crystal break plane.

The Kikuchi sphere in **Fig. 24** shows the orientation of the sample that is in agreement with indistinct cleavage of fluorapatite to the direction given by Miller-Bravais indices of $\{0001\}$.

3.3. Thermodynamic properties of apatite

DROUET [170] gives the comprehensive review on experimental and predicted thermodynamic properties of phosphate apatites and oxyapatites, where O^{2-} ion replaces $2X^-$ in general $M_{10}(PO_4)_6X_2$ formula of apatite phase and publishes the summary of available thermodynamic data including standard formation Gibbs energy (ΔG_f°), ΔH_f° and S° at the temperature of 298 K (25°C) and the pressure of 1 bar (10^5 Pa), which are listed in the periodic table of phosphate apatites in Fig. 25.

**Periodic Table of Phosphate Apatites $M_{10}(PO_4)_6X_2$:
Recommended Thermodynamic Properties
(298 k, 1 bar)**

oxyapatite		s-block cations				d-block cations				p-block cations			
	Ca^{2+} O^{2-}	Mg^{2+} OH^-	Mg^{2+} F^-	Mg^{2+} Cl^-	Mg^{2+} Br^-	Cu^{2+} OH^-	Cu^{2+} F^-	Cu^{2+} Cl^-	Cu^{2+} Br^-	Pb^{2+} OH^-	Pb^{2+} F^-	Pb^{2+} Cl^-	Pb^{2+} Br^-
Mg	-12290 -13066 634	-11522 -12337 634	-11714 -12495 618	-11447 -12219 676	-11421 -12162 700	-6524 -7309 741	-6709 -7460 719	-6450 -7187 797	-6424 -7127 829	-7550 -8286 1222	-7647 -8360 1163	-7522 -8212 1274	-7520 -8180 1293
Ca	-12634 -13432 780	-12899 -13658 778	-12434 -13185 835	-12346 -13063 870		-8623 -9380 919	-8808 -9532 897	-8549 -9258 976	-8523 -9198 1008				
Sr	-12587 -13373 954	-12845 -13604 912	-12478 -13233 956	-12487 -13201 1013									
Ba	-12553 -13309 1130	-12834 -13564 1084	-12529 -13246 1158	-12472 -13154 1194		-7873 -8650 952	-8045 -8795 910	-7719 -8463 960	-7702 -8405 1019				

M^{2+} X^-
 ΔG_f°
 ΔH_f°
 S°

Regular lettering: averaged data from literature (see Table 1)
Italic lettering: best estimated values from Drouet (this paper)
 Estimated relative error: within 1%

From C. Drouet (2014)
Journal of Chemical Thermodynamics (JCT)

Fig. 25. Comprehensive periodic table of phosphate apatites provided by C. DROUET [170].

The discrepancies between published thermodynamic data probably arise from variable crystallinity states, polymorphs (either hexagonal or monoclinic, those not being systematically identified in literature reports), nonstoichiometry, hydration state and/or the presence of undetected impurities. When experimental-based data are not available (or are questionable), the so-called prediction of thermodynamic properties of solids becomes relevant. For example, it may allow an understanding of some unsuccessful experiment aiming at obtaining a desired hypothetical composition, or it may fill the gap between reported and needed thermodynamic values for the evaluation of equilibria constants or for the establishment of phase diagrams [170]. There are many methods developed for this purpose the summary of which can be found in works [171],[172].

For double oxides, $A_xB_yO_z$ in the system AO-BO was established the dependence [171]:

$$\Delta H_{f,cc}^\circ = (A_xB_yO_z) = f(\Delta \bar{H}_f^\circ) \quad (15)$$

where $\Delta H_{\text{fcc}}^\circ(\text{A}_x\text{B}_y\text{O}_z)$ is the standard enthalpy of the formation of double oxide $\text{A}_x\text{B}_y\text{O}_z$ from the component oxides AO and BO and $\Delta \bar{H}_f$ represents the sum of molar fraction enthalpies of component oxides AO and BO according to the following relationship:

$$\Delta \bar{H}_f^\circ = x_{\text{AO}} \Delta H_f^\circ(\text{AO}) + x_{\text{BO}} \Delta H_f^\circ(\text{BO}) \quad (16)$$

$\Delta H^\circ(\text{AO})$ and $\Delta H^\circ(\text{BO})$ are the standard enthalpies of the formation of component oxides from the elements, and X_{AO} and X_{BO} are the molar fractions of component oxides in the double oxide $\text{A}_x\text{B}_y\text{O}_z$ with a given composition [171].

The entropy of a solid compound is a function of masses of constituent atoms and the forces acting between these atoms: the greater the mass and the lower the force, the larger the entropy. The entropy of ionic solid will also depend upon the magnitude of the ionic charges. For compounds, the specific heat of which has reached the DULONG and PETIT [173] value of 6 cal. per gram-atom [174],[175],²⁷ the mass is the principal factor, and in 1921, the authors gave an equation for the contribution of each element to the entropy of the compound [176].

$$S^\circ(298 \text{ K}) = \frac{3}{2} R \ln \text{at. wt.} - 0.94 \quad (17)$$

For simple salts, such as alkali halides, the entropy may be estimated with fair accuracy as the sum of the entropies of constituent elements as given by this equation. However, the forces in solid salts are largely the ionic attractions, and the effect of the ionic radii upon the force constants and the vibrational frequencies is appreciable; in general, the entropy of a large ion is increased and the entropy of a small ion is decreased compared to the values given by Eq. 17. [176].

3.3.1. Volume-based thermodynamic predictive method

The volume-based thermodynamic approach (VTB), the so-called first-order method, has especially received much attention because the method is rather easy to use and has been shown in some cases to lead to output data well related to experimental results [170].

²⁷ One calorie is 4.184 J (joules). Gram-atom [gm] (and gram-molecule) was used to specify the amount of chemical elements or compound. These units had a direct relation with "atomic weights" and "molecular weights," which are in fact relative masses. "Atomic weights" were originally referred to the atomic weight of oxygen, by general agreement taken as 16. Although physicists separated the isotopes in a mass spectrometer and attributed the value of 16 to one of the isotopes of oxygen, chemists attributed the same value to the (slightly variable) mixture of isotopes 16, 17, and 18, which was for them naturally occurring element oxygen. Finally, an agreement between the International Union of Pure and Applied Physics (IUPAP) and the International Union of Pure and Applied Chemistry (IUPAC) brought this duality to an end in 1959/1960. Physicists and chemists have ever since agreed to assign the value 12, exactly, to the so-called atomic weight of the isotope of carbon with the mass number 12 (carbon 12, ^{12}C), correctly called the relative atomic mass $A_r(^{12}\text{C})$. The unified scale thus obtained gives the relative atomic and molecular masses, also known as the atomic and molecular weights, respectively [174]. The law is also known as Dulong and Petit principle, which can be expressed in modern unit as: atomic weight $\times$ specific heat $\approx \partial(3kTN_A)/\partial T \approx 3kN_A \approx c_v \approx 25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, i.e. the atomic weight of solid element multiplied by its molar specific heat is a constant [175].

3.3.2. Additive estimation methods

Additive estimation or contributive methods are probably the simplest approach based on the following [170],[177]:

1. **Atomic and ionic contribution:** the technique based on the method proposed by KELLOGG [178]:

$$\begin{aligned} C_{\text{pm}}^{\circ}(A_x B_y, 298.15 \text{ K}) &= x C_{\text{pm}}^{\circ}(A) + y C_{\text{pm}}^{\circ}(B) \quad \text{e.g.:} \\ C_{\text{pm}}^{\circ}(\text{BaCl}_2, 298.15 \text{ K}) &= C_{\text{pm}}^{\circ}(\text{Ba}) + 2 C_{\text{pm}}^{\circ}(\text{Cl}) \end{aligned} \quad (18)$$

The approach was later revised by KUBASCHEWSKI [179],[180]. These authors also proposed the method for the estimation of parameters A, B and C in the temperature dependence of $C_{\text{pm}}^{\circ}(T)$ ²⁸:

$$C_{\text{pm}}^{\circ}(T) = A + BT + \frac{C}{T^2} \quad (19)$$

$$A = \frac{10^{-3} T_m [C_{\text{pm}}^{\circ}(298.15 \text{ K}) + 4.7n] - 1.25n \cdot 10^5 (T_m)^{-2} - 9.05n}{10^{-3} T_m - 0.298} \quad (20)$$

$$B = \frac{25.6n + 4.2n \cdot 10^5 (T_m)^{-2} - C_{\text{pm}}^{\circ}(298.15 \text{ K})}{10^{-3} T_m - 0.298} \quad (21)$$

$$C = -4.2n \quad (22)$$

where n is the number of ions (contributions) in the formula unit. The described approach is worthy for the substances with melting point temperatures (T_m) bellow 2300 K. The data on cationic and anionic contributions to heat capacity at 298 K are published in works [177], [179],[181],[182],[183].

For ionic compounds, the entropy can be calculated²⁹ from additive data given in **Table 4**, empirically found for cation and anion constituents of the compound (increments method of LATIMER [184]) [172].

	Element	C_{pm}°	S_m°	Element	C_{pm}°	S_m°	Element	C_{pm}°	S_m°
Contribution of cations	Ag	25.76	57.6	Hf	25.52	53,0	Pr	24.27	61.1

²⁸ The full equation for the temperature dependence is $C_{\text{pm}}^{\circ} = A + BT + C/T^2 + DT^2 + F/T^{1/2}$ [J·K⁻¹·mol⁻¹].

	Element	C _{pm} [°]	S _m [°]	Element	C _{pm} [°]	S _m [°]	Element	C _{pm} [°]	S _m [°]
[J·K ⁻¹ ·mol ⁻¹]									
	Al	19.66	23.4	Hg	25.10	59.4	Rb	26.36	59.2
	As	25.10	45.2	Ho	23.01	56.0	Sb	23.85	58.9
	Au	–	58.5	In	24.27	55.0	Se	21.34	60.5
	B	–	23.5	Ir	(23.85)	50.0	Si	–	35.2
	Ba	26.36	62.7	K	25.94	46.4	Sm	25.10	60.2
	Be	(9.62)	12.6	La	(25.52)	62.3	Sn	23.43	58.2
	Bi	26.78	65.0	Li	19.66	14.6	Sr	25.52	48.7
	Ca	24.69	39.1	Lu	–	51.5	Ta	23.01	53.8
	Cd	23.01	50.7	Mg	19.66	23.4	Te	–	69.0
	Ce	23.43	61.9	Mn	23.43	43.8	Th	25.52	59.9
	Co	28.03	34.1	Mo	–	35.9	Ti	21.76	39.3
	Cr	23.01	32.9	Na	25.94	37.2	Tl	27.61	72.1

²⁹**Table 4** [172] refers to the values of entropy contribution from work [176] where some data for PO₄³⁻ ion are given in brackets. In order to verify this value (for the charge of cation, i.e. Ca²⁺, the contribution of PO₄³⁻ anion is 17 [calories] × 4.184 = 71.13 J·K⁻¹·mol⁻¹, it is possible to calculate it from recommended thermodynamic data from **Fig. 25**. If (for example) three apatite end members were used, it is possible to calculate the contribution to PO₄³⁻ anion in hydroxylapatite, fluorapatite, chlorapatite, and bromapatite as follows:

$$\text{HAP: } (10 \cdot 39.1) + (6x) + (2 \cdot 18.83) = 780 \Rightarrow x = 58.56 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\text{FAP: } (10 \cdot 39.1) + (6x) + (2 \cdot 17.00) = 728 \Rightarrow x = 50.50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\text{ClAP: } (10 \cdot 39.1) + (6x) + (2 \cdot 31.80) = 835 \Rightarrow x = 63.40 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\text{BrAP: } (10 \cdot 39.1) + (6x) + (2 \cdot 45.70) = 870 \Rightarrow x = 64.60 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

It is also possible to calculate it from the contribution data for Ca₃(PO₄)₂ or Mg₃(PO₄)₂, where S°(298.15K) = 235.998 and 189.2 J·K⁻¹mol⁻¹ (HSC software v.7.1), respectively:

$$(3 \cdot 39.1) + (2x) = 235.998 \Rightarrow x = 59.35 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$(3 \cdot 23.40) + (2x) = 189.2 \Rightarrow x = 59.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Therefore, it is suggested to use average value from these calculations, i.e. PO₄³⁻ (for M²⁺ cation) ≈ 59 J·K⁻¹mol⁻¹. It is then possible that the application of contribution techniques to apatite leads to positive error in estimated thermodynamic data.

	Element	C_{pm}°	S_m°	Element	C_{pm}°	S_m°	Element	C_{pm}°	S_m°
	Cs	26.36	67.9	Nb	23.01	48.1	U	26.78	64.0
	Cu	25.10	44.0	Nd	24.27	60.7	V	22.18	36.8
	Fe	24.94	35.0	Ni	(27.61)	35.1	Y	(25.10)	50.4
	Ga	(20.92)	40.0	Os	–	50.0	Zn	21.76	42.8
	Gd	23.43	56.0	P	14.23	39.5	Zr	23.85	37.2
	Ge	20.08	49.8	Pb	26.78	72.2	–	–	–
	Anion	C_{pm}°	S_m° for oxidation charge of cation						
			I	II	III	IV			
Contribution of anions J·K ⁻¹ ·mol ⁻¹]	H ⁻	8.79	–	–	–	–			
	F ⁻	22.80	20.8	17.0	18.3	20.4			
	Cl ⁻	24.69	36.3	31.8	30.3	34.4			
	Br ⁻	25.94	50.3	45.7	44.7	50.8			
	I ⁻	26.36	58.3	53.5	54.8	53.9			
	O ²⁻	18.41	4.5	2.9	2.4	3.2			
	S ²⁻	24.48	20.6	18.4	20.1	17.0			
	Se ²⁻	26.78	35.5	32.8	34.1	30.9			
	Te ²⁻	27.20	38.1	41.9	44.1	40.1			
	OH ⁻	30.96	(20.9)	(18.8)	(12.6)	–			
	SO ₄ ²⁻	76.57	80.0	69.5	64.2	(41.8)			
	SO ₃ ²⁻	–	42.9	–	–	–			
	NO ₃ ⁻	64.43	86.0	74.0	–	–			
	NO ₂ ⁻	–	70.6	–	–	–			
	CO ₃ ²⁻	58.58	62.4	46.6	–	–			
	CrO ₄ ²⁻	90.76	–	–	–	–			
	MoO ₄ ²⁻	90.37	–	–	–	–			
	WO ₄ ²⁻	97.49	–	–	–	–			
	SiO ₃ ²⁻	59.3	60.7	43.9	29.3	–			
	SiO ₄ ⁴⁻	73.5	–	–	–	–			
	PO ₄ ³⁻	73.90	(100.4)	(71.1)	(50.2)	–			
	UO ₄ ²⁻	107.11	–	–	–	–			

Table 4. The contribution of cations and anions to C_{pm}° and S_m° (298.15 K) [172],[180].

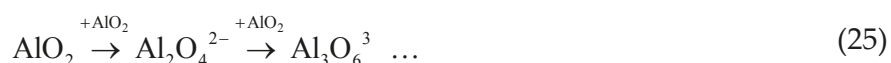
2. **Structural and simple oxide contribution:** the value of $C_{\text{pm}}^\circ(298.15 \text{ K})$ or the parameters of the temperature dependence in Eq. 19 can be calculated from the contribution of constituent oxides (Neumann–Kopp rule, NKR):

$$x A(s) + y B(s) = A_x B_y(s), \quad \text{e.g., } \text{SrO}(s) + \text{CuO}(s) = \text{SrCuO}_2(s) \quad (23)$$

$$\begin{aligned} C_{\text{pm}}^\circ(A_x B_y, 298.15 \text{ K}) &= x C_{\text{pm}}^\circ(A, 298.15 \text{ K}) + y C_{\text{pm}}^\circ(B, 298.15 \text{ K}) \quad \text{e.g.,} \\ C_{\text{pm}}^\circ(\text{SrCuO}_2, 298.15 \text{ K}) &= C_{\text{pm}}^\circ(\text{SrO}, 298.15 \text{ K}) + C_{\text{pm}}^\circ(\text{CuO}, 298.15 \text{ K}) \end{aligned} \quad (24)$$

or from the structural contribution [179].

3. **Prediction method for homological series and groups of chemically related substances (oxides):** based on the approach of ALDABERGENOV et al [185] and GOSPODINOV and MIHOV [186]. The molar heat capacity in homological series as $A_m(\text{B}_x\text{O}_y)_n$ is a linear function of n , i.e. the coefficient which specifies the number of complex anions $(\text{B}_x\text{O}_y)^{z-}$ in the formula unit. For example, for the series of alkaline aluminate, it can be written as



Since each higher anion is formed by the addition of primary ion $(\text{AlO}_2)^-$ unit, higher anion is considered to form n -multiples of primary ion, the value of which is determined from the available experimental data for KAlO_2 , LiAlO_2 and NaAlO_2 and from ions contribution for cation K^+ , Li^+ and Na^+ obtained from their standard entropies in an infinitely diluted solution [179].

Apatite phase may be treated in the first approximation as the sum of contributions arising from the constitution of binary oxides/compounds. For example, in the case of fluorapatite $(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2)$, a decomposition into contribution of $9\text{CaO} + 3\text{P}_2\text{O}_5 + \text{CaF}_2$ could be considered. It can be generalized to any end-member in the form $9\text{CaO} + 3\text{P}_2\text{O}_5 + \text{XF}_2$ [170].

3.4. Dissolution of apatites

At the fundamental level, the reactions between solids and liquids involve a coupled sequence of mass transport, adsorption/desorption phenomena, heterogeneous reactions, chemical transformations of intermediates, etc., the identification, separation and kinetic quantification of which are all necessary if the mechanism of the process is to be fully understood and described [111],[187]. It was generally accepted that the process during the dissolution of lattice ions includes the following [187],[188]:

- a. Detachment of species (ion) from a kink site

- b. Surface diffusion from the crystal steps
- c. Desorption from the surface
- d. Diffusion into the bulk solution

The dissolution of apatites under steady-state conditions, in pure water or in aqueous acidic media, includes the following simultaneous steps [187],[189]:

- i. Diffusion of chemical reagents (H^+) from bulk solution to the solid/liquid interface. In the case of acidic dissolution, the diffusion of acid anions (A^{n-}) must be taken into account as well.
- ii. Adsorption of H^+ onto the surface of apatite.
- iii. Chemical transformation of the surface.
- iv. Desorption of ions of fluoride, calcium and phosphate from the crystal surface.
- v. Adsorption of chemicals from solution back onto the surface of apatite.

These steps are likely to be more complicated, e.g. the processes I and V include chemical transformation of ionic species during diffusion because the pH of solution is known to depend on the distance from the solid/liquid interface. In other words, the value of pH is higher near to the surface of apatite and decreases with increasing distance from the surface.

When apatite gets in contact with undersaturated solution, the dissolution states from 1 to 5 mentioned above take place. In order to provide detailed description of the process, the following assumption must be introduced [187]:

- a. Stoichiometric apatite is dissolved, and neither nonstoichiometric layer nor other ions except for calcium, phosphate, hydroxide and fluoride are initially present in the crystal lattice, whereas the volume and surface defects (dislocations and dislocations outlets, respectively) might be present and, when present, they are distributed randomly.
- b. Except for the presence of dislocation outlets, the initial surface of apatite is perfect (molecularly sooth). Otherwise, each imperfection might be the dissolution nucleus.
- c. Despite the limitations and drawbacks discussed above, all models are correct and complementary to each other.
- d. In some cases, anions of acid might have an influence on apatite dissolution due to the specific affinity (e.g. citrate) by means of formation of insoluble compounds (e.g. sulfate). That is the reason why anions are not specified either here or below. It is just assumed that the dissolution of apatite happens in acid H_nA , where A^{n-} is an anion.
- e. The hydration effect on all ions and molecules involved as well as that on crystal surface of apatite is omitted for simplicity.
- f. All crystal faces of solid apatite are equal and have similar ionic arrangement. There is not any considered specific influence of different crystal faces on the dissolution mechanism.

Since the dissolution models have limitations and drawbacks, none of them was able to describe the dissolution of apatite in general. Furthermore, the most of models were elaborated for the apatite dissolution in slightly acidic or nearly neutral solution ($4 < \text{pH} < 8$), for relatively small values of solution undersaturation and for the temperatures in the range from 25°C to 37°C , nothing is known about their validity for the dissolution of apatite in strong inorganic acid such as HCl , HNO_3 and H_2SO_4 and at temperatures above 70°C [187].

The classification of congruent (stoichiometric)/incongruent (nonstoichiometric) dissolution is based on direct measurements of either ionic concentrations in the solution or the surface composition of apatite during the dissolution [187]:

1. **Congruent dissolution:** ions in solids are dissolved simultaneously with the dissolution rates proportional to their molar concentrations, e.g. for $\text{Ca}_5(\text{PO}_4)_3\text{Z}$ it should be written [190],[191]:

$$\frac{[\text{Ca}]_t}{[\text{P}]_t - [\text{P}]_0} - R = 0 \quad (26)$$

where $[\text{Ca}]_t$, $[\text{P}]_t$ and $[\text{P}]_0$ denotes actual (at time t) concentration of calcium and phosphorus in the solution and initial concentration of phosphorus (at time $t = 0$), respectively. The value of R is given by ideal stoichiometric ratio of $\text{Ca:P} = 5/3$ in the formula of apatite (Table 7 in Chapter 1).

2. **Incongruent dissolution:** the dissolution rate is different for each ion. That leads to the formation of surface layer with chemical composition different from the bulk of solid apatite phase.

The behavior of surface of apatite during the dissolution according to DOROZHKIN [112] is shown in Fig. 26. Fluorine from fluorapatite or hydroxyl from hydroxyapatite dissolves most probably as the first. This can be explained by their position in the channels of crystal lattice. The dissolution starts with replacements of fluorine for water. Proton(s), chemisorbed on the nearest phosphate group(s), most probably catalyze this process. Local positive charge on apatite is formed as the result (b). Obtained local positive charge is removed by the detachment of one of the nearest calcium cations: $\text{Ca}(2)$ is more likely to be detached first (c) since $\text{Ca}(1)$ is located rather far from the channel. Acidic anions present in the solution most probably participate in this process. Later, proton(s) from the bulk solution replace other calcium cation(s) around the nearest phosphate group. Very thin surface layer of acidic calcium phosphates is formed as the result [112].

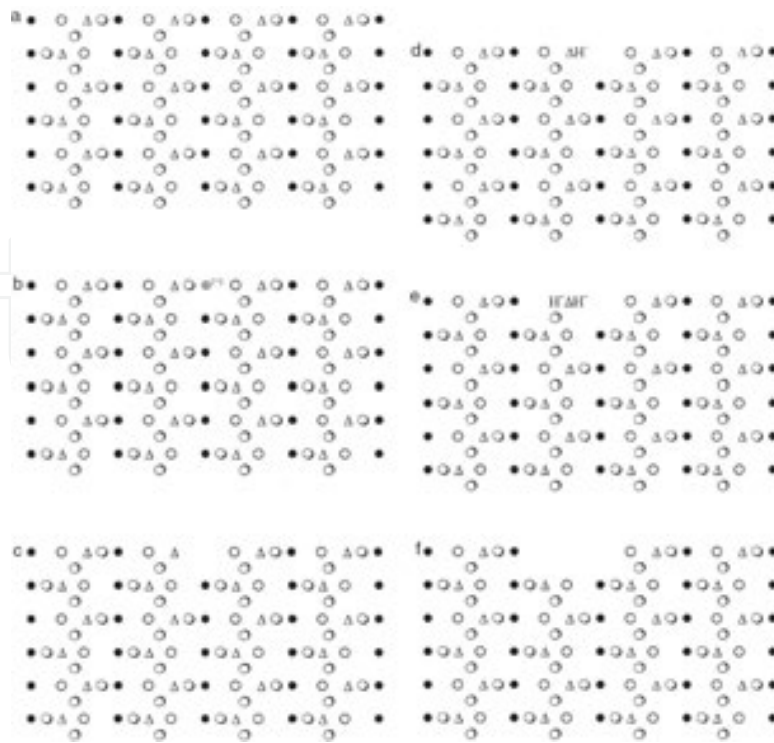


Fig. 26. Schematic illustration of the surface dissolution mechanism of apatite at the nanolevel: (a) part of the initial surface of apatite; (b) replacement of one fluorine (or hydroxyl) anion with water molecule resulting in local positive charge formation; (c) removal of one of the nearest calcium cations; (d) sorption of next proton; (e) removal of another calcium cation with simultaneous formation of acidic calcium phosphate; (f) detachment of one phosphate anion together (or simultaneously) with third calcium cation. A jump-wise shift of the dissolution step occurs simultaneously at stage f. (●) Fluorine for fluorapatite or hydroxyl for hydroxylapatite; (○) Ca(II) on the first plane, (○) Ca(II) on the back plane and Ca(I) on the back plane; (*) molecule of water and local positive charge; (Δ) PO_4^{3-} tetrahedra; $\text{H}^+\Delta\text{H}^+$ and ΔH^+ represent the surface tetrahedral anions of H_2PO_4^- and HPO_4^{2-} , respectively. Chemisorbed protons, water molecules and acidic anions are omitted for simplicity. Note that crystal structure of apatite is shown very schematically: it should be hexagonal, while here it looks more or less like cubic [112].

When all (or almost all) the nearest calcium cations have been replaced with protons according to the reactions [112]:

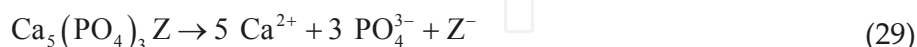


phosphate anions (H_2PO_4^- , $\text{CaH}_2\text{PO}_4^+$, or H_3PO_4) also detach (f). As the result, the dissolution step moves forward jump-wise over a distance equal to the dimension of phosphate anion, of approximately 3 Å. The detachment of phosphate anions and calcium cations results in the formation of hole. The dimension of this hole should be close to the lattice parameters of apatite. Most probably, it is a dissolution nucleus on which the polynuclear dissolution mechanism is based [112].

3.4.1. Dissolution of fluorapatite

The adsorption of H^+ onto the surface of apatite (**Fig. 26(b)–(d)**) resulted in the aqueous pH increasing from 5.60 to 8.45 within the first hour of dissolution. Ions of H^+ were adsorbed onto oxygen ions of phosphate groups as well as onto ions of fluoride [187],[191].

The reaction of stoichiometric (congruent) dissolution of pure stoichiometric apatite can be expressed by the reaction³⁰ [112],[187],[192]:



where $Z = OH^-$ and F^- . Assuming the unit activity of the solid phase ($a_{Ca_5(PO_4)_3Z} = 1$), the equilibrium constant of dissolution (K) can be expressed via the solubility product or ion activity product (IAP) of apatite³¹ [187],[193],[194],[195],[196]:

$$K = IAP = a_{Ca^{2+}}^5 a_{PO_4^{3-}}^3 a_Z \quad [eq.] \quad (30)$$

where a_i denotes the thermodynamic activity of aqueous species. The standard Gibbs (free) energy of the reaction related to the standard temperature (298.15 K) and pressure (0.101 MPa) is given by the formula³²:

³⁰ Reaction **Eq. 7** and **Eq. 12** are widely used for the description of dissolution process of apatite [112] using stoichiometry pertinent single or double apatite formula and $Z = F$ or OH .

³¹ Out of equilibrium state, IAP is not equal to K (see the discussion to **Eq. 20**). Double formula of apatite is assumed then with respect to the apatite stoichiometry; the law for ionic activity product has the following form:

$$K_{sp} = a_{(Ca^{2+})}^{10} a_{(PO_4^{3-})}^6 a_{(Z^-)}^2.$$

For example, in hydroxylapatite, where $Z^- = OH^-$, the activity of OH^- anion can be expressed by using ionic product of water (25°C): $K_w = a_{(H^+)} a_{(OH^-)} = 1 \cdot 10^{-14} \text{ (mol} \cdot \text{dm}^{-3})^2$ and then $a_{(OH^-)} = K_w / a_{(H^+)}$. Since $pH = -\log [H^+]$ and $pOH = -\log [OH^-]$ the $[H^+] = 10^{-pH}$ and $[OH^-] = 10^{-pOH}$ and $pK_w = pH + pOH = 14$:

$$K_{sp} = a_{(Ca^{2+})}^{10} a_{(PO_4^{3-})}^6 10^{-2pOH} = a_{(Ca^{2+})}^{10} a_{(PO_4^{3-})}^6 10^{-2(14-pH)} = a_{(Ca^{2+})}^{10} a_{(PO_4^{3-})}^6 K_w^{-2} 10^{2pH}.$$

The activity of ionic species is the product of ion molar concentration ([196]) and ion activity coefficient, e.g. ($a_{(Ca^{2+})} = ([Ca^{2+}] / [Ca^{2+}]^\circ) \gamma_{Ca^{2+}}$, where the standard state $[Ca^{2+}]^\circ = 1 \text{ mol} \cdot \text{dm}^{-3}$ can be chosen), which can be calculated, e.g. the example via **Debye–Hückel**, **extended Debye–Hückel**, or **modified Davies equation** (in dependence on ionic strength):

$$\log \gamma_i = -AZ_i^2 \sqrt{I} \quad (I < 10^{-3}),$$

$$\log \gamma_i = [-AZ_i^2 \sqrt{I} / (1+B \cdot \alpha_i \sqrt{I})] \quad (10^{-3} < I < 0.1),$$

$$\text{or } \log \gamma_i = [-AZ_i^2 \sqrt{I} / (1+B \cdot \alpha_i \sqrt{I})] + 0.3I \quad (I > 0.1), \text{ respectively.}$$

A and B are the temperature-dependent constants, Z_i is the charge number of i th ion, α_i is the radius of hydrated i th ion, and I is the number of ions: $I = \frac{1}{2} \sum ([C_i] Z_i^2)$.

The solubility product defined as the product of concentration of compound constituents ions, which are released during the dissociation is often used: $K_{sp} = [Ca^{2+}]^{10} [PO_4^{3-}]^6 [Z^-]^2$.

³² $\Delta_r G^\circ = -RT \ln K$ (in the equilibrium state) and $\ln K = \ln 10 \log K$. From that, it should be derived that $\Delta_r G^\circ = -8.314 \cdot 298.15 \ln 10 \log K = -5708 \log K \text{ [J} \cdot \text{mol}^{-1}]$, where $\ln 10 \approx 2.303$. Since $\log_{10} K = \log K = \lg K$, it can also be written as $\Delta_r G^\circ = -5708 \lg K$.

$$\Delta_r G^\circ = -5.707 \log K \quad \left[\text{kJ} \cdot \text{mol}^{-1} \right] \quad (31)$$

For reaction 29, the following equation³³ can be derived [187]:

$$\begin{aligned} \Delta_r G^\circ = & 5 \Delta G_f^\circ(\text{Ca}^{2+}) + 3 \Delta G_f^\circ(\text{PO}_4^{3-}) + \Delta G_f^\circ(\text{Z}^-) \\ & - \Delta G_f^\circ(\text{Ca}_5(\text{PO}_4)_3\text{Z}) \end{aligned} \quad (32)$$

Eq. 32 can be further treated as follows:

$$\begin{aligned} \Delta G_f^\circ(\text{Ca}_5(\text{PO}_4)_3\text{Z}) = & 5 \Delta G_f^\circ(\text{Ca}^{2+}) + 3 \Delta G_f^\circ(\text{PO}_4^{3-}) \\ & + \Delta G_f^\circ(\text{Z}^-) - \Delta_r G^\circ \end{aligned} \quad (33)$$

HAROUTYA et al [197] assumes that the dissolution of apatite in the temperature range from 5°C to 50°C, and the pH from 1 to 6 can be expressed by the following formula:



With regard to assumed standard state, the equilibrium constant of reaction (Eq. 34) can be written as³⁴

$$K' = a_{\text{Ca}^{2+}}^5 a_{\text{HPO}_4^{2-}}^3 a_{\text{F}^-} a_{\text{H}^+}^{-3} \quad (35)$$

The chemical affinity³⁵ (*A*) of Eq. 34 is given by the law:

$$A = -RT \ln \left(\frac{K' a_{\text{H}^+}^3}{a_{\text{Ca}^{2+}}^5 a_{\text{HPO}_4^{2-}}^3 a_{\text{F}^-}} \right) \quad (36)$$

In the closed-system experiment, the dissolution rates are generally obtained from the slope of concentration of reactive solution versus the time:

³³ $\Delta_r G^\circ = \sum \nu_i \Delta G_{f,i}^\circ$ where ν_i denotes the stoichiometric coefficient of given species and $\Delta G_{f,i}^\circ$ its standard enthalpy of formation.

³⁴ Since the saturation of solution with respect to $\text{Ca}_5(\text{PO}_4)_3\text{Z}$ means that $K' = 0$ (equilibrium state), it can be derived that $a_{\text{Ca}^{2+}}^5 a_{\text{PO}_4^{3-}}^3 a_{\text{Z}^-} - K' a_{\text{H}^+}^3 = 0$ and then $\Delta_r G^\circ = -RT \ln (a_{\text{Ca}^{2+}}^5 a_{\text{PO}_4^{3-}}^3 a_{\text{Z}^-} / K' a_{\text{H}^+}^3)$. Since $A = -\Delta_r G^\circ$ (please see note 35), $A = -RT \ln (K' a_{\text{H}^+}^3 / a_{\text{Ca}^{2+}}^5 a_{\text{PO}_4^{3-}}^3 a_{\text{Z}^-})$.

³⁵ The relationship between the reaction Gibbs energy and chemical affinity: $A = -\Delta_r G^\circ$ was introduced by T. DE DONDER.

$$r = \frac{\partial c_i}{\partial t} \frac{M_r}{v_i s} \quad (37)$$

where r refers to the dissolution rate of apatite, c_i denotes the concentration of i th element, t is the time, M_r designates the mass of fluid in the reactor, v_i is the stoichiometric coefficient and s designates the total surface area of sample in the reactor. The slope of the plot may not be constant and may increase or decrease with time from the following reasons [195],[197]:

1. Changes in the reactive fluid volume, which may occur due to the evaporation of solvent or regular sampling of reactive fluid
2. Nonzero order reaction kinetics
3. Approach to equilibrium, where the dissolution rate decreases and reaches zero at equilibrium. This approach is described by the transition state theory as follows:

$$r = r_+ \left(1 - \exp \left[\frac{-A}{\sigma RT} \right] \right) \quad (38)$$

The symbol r_+ symbolizes the far from equilibrium dissolution rate, which may depend on the composition of solution, A is the affinity of reaction of dissolution, σ stands for the Temkin's average stoichiometric number equal to the ration of rate of destruction of the activated or precursor complex relative to overall rate, R designates universal gas constant and T is the temperature on the absolute scale. Overall rate (r) is equal to forward rate (r_+) when $A \gg \sigma RT$. As one of the approaches of equilibrium, overall rates gradually decrease and reach zero at equilibrium where $A = 0$. The value of r is within 10% of r_+ when $A/\sigma RT > 2.3$ which is equivalent to $A > 1.36 \sigma \text{ kcal} \cdot \text{mol}^{-1}$. It indicates that the parameter σ plays a crucial role in the variation of dissolution rates at near to equilibrium conditions [195],[197].

The value of r_+ depends on the pH according to the following equation [197],[198]:

$$r_+ = k \text{ pH}^{-n} \quad (39)$$

where k refers to the tare constant and n stands for the reaction order determined as the slope of linear dependence of $\ln r_+$ on pH. The dependence of k on the temperature is given by the Arrhenius law:

$$k = A_A \exp \left(\frac{-E_A}{RT} \right) \quad (40)$$

where A_A is the preexponential (frequency) factor and E_A is the activation energy of the process. The combination of Eqs. 38, 39 and 40 leads to the equation for the dissolution rate as follows [197]:

$$r = A_A a_{H^+}^n \exp(E_A / RT) \left(1 - \exp \left[\frac{-A}{\sigma RT} \right] \right) \quad (41)$$

For acidic dissolution of calcium fluorapatite, ions of F were found to dissolve faster (or prior to) when compared to calcium and phosphate. A similar phenomenon of prior (or faster) dissolution of calcium when compared to that of phosphate was also found [187],[199]. The release of calcium and phosphate ions from the surface of apatite seems to be affected by the presence of salts, such as Na_2SO_4 , CH_3COONa , or $NaCl$, in the solution. The concentration of phosphate in the solution increases in the following order [187]:



On the contrary, the concentration of calcium ions decreases in the same order.

The undersaturation (US) and relative undersaturation (US_r) of apatite solvent dissolved upon is defined as follows³⁶ [193]:

$$US_r = 1 - US = 1 - \left(\frac{IAP}{K} \right)^{1/18} \quad (42)$$

where K is the equilibrium constant of reaction 29 and IAP is the ion activity product. The law is written with regard to the stoichiometry of double formula of apatite, where $\sum \nu_i$ in Eq. 30 is $2 \times (5 + 3 + 1) = 18$. The value of IAP/K ratio is as follows:

- a. $IAP/K > 1$, the reaction proceeds to the left (precipitation, supersaturated solution)
- b. $IAP/K = 1$, the reaction is in the equilibrium state (saturated solution)
- c. $IAP/K < 1$, the reaction proceeds to the right (dissolution, undersaturated solution)

This ratio is also used to calculate the saturation index (SI) for the reaction of dissolution [200]:

$$SI = \log \left(\frac{IAP}{K} \right) \quad (43)$$

Depending on the saturation index, the following states of solutions are recognized:

³⁶ Since the system is not in the equilibrium state $IAP \neq K$.

- i. $SI < 0$ undersaturation
- ii. $SI = 0$ saturation, i.e. mineral³⁷ or salt is in equilibrium with solution
- iii. $SI > 0$ supersaturation

3.4.2. Classification of the dissolution models

The models, which are usually applied for the description of dissolution of apatites, include the following [187]:

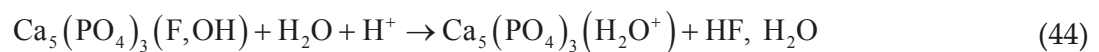
1. **Diffusion and kinetically controlled models:** the dissolution of apatite was found to be the diffusion (transport) controlled in some cases [201],[202], kinetically (surface) controlled in other ones [203],[204], and even intermediate [205], i.e. both diffusion and kinetically controlled. Both models usually operate with the so-called driving force which means either the concentration gradient within the Nernst diffusion layer (the diffusion controlled model) or the gradient of ionic chemical potentials between the apatite crystal surface and bulk solution (the kinetically controlled model). Moreover, the results obtained on these models are valid only within the experimental conditions studied; no extrapolation can be made beyond the tested ranges. For example, after, let's say, a slight agitation decrease or temperature increase, an initially kinetically controlled dissolution might be controlled by the diffusion. Thus, high sensitivity to applied experimental conditions appears to be the main drawback of these models [187].
2. **Polynuclear model:** is based on the study of dissolution and kinetics of growth of apatite under constant composition conditions [191],[193],[206],[207],[208]. Polydispersed samples of apatite were put into a stirred undersaturated (for dissolution experiments) or supersaturated (for those on crystal growth) solutions, and the pH of solution and the amount of added chemicals (an acid for the dissolution experiments and a base for those on crystal growth) were permanently recorded as the functions of time. The results obtained were plotted versus either undersaturation or supersaturation values: straight lines were obtained in the specific logarithmic coordinates typical for this model. According to the model, the dissolution nuclei, i.e., the collections of vacant sites for Ca^{2+} , PO_4^{3-} , and OH^- ions, are formed on the crystal surface of apatite and spread over the surface with a definite lateral rate.

The nucleation rate is assumed as a function of mean ion activity. The lateral growth rate of nuclei is assumed proportional to the difference between total concentration of calcium ions in the saturated solution and in a solution, while the rate constant is related to the frequency for calcium ions to make a diffusion jump into a kink and, simultaneously, partly dehydrate. Recent investigation reveals that the rate-determining step was not the diffusion but two-dimensional surface nucleation [187].
3. **Self-inhibition model:** assumes the formation of self-inhibition calcium-rich layer on the surface of apatite during the dissolution. According to this model, apatite is dissolved by

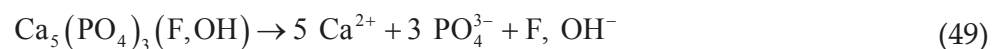
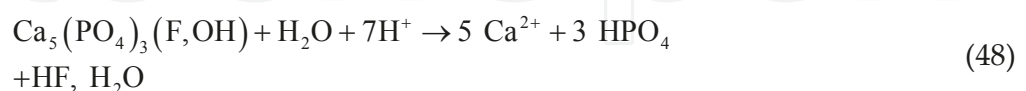
³⁷ The ranges of SI near zero are generally considered to be within the equilibrium zone for the mineral. The ranges of $SI = 0 \pm 0.5$ and $0 \pm (5\%)$ ($\lg K_{\text{mineral}}$) were used in various studies [200].

ionic detachment of calcium and phosphate ions from the surface to a solution. When an initial portion of apatite has been dissolved, some amount of calcium cations (probably, in connection with anionic counter ions) is returned from the solution and adsorbed back onto the surface of apatite. The latter process results in the formation of a semipermeable ionic membrane, which is formed from positively charged layer containing strongly adsorbed calcium ions, i.e. calcium-rich layer [187], [201],[209],[210],[211].

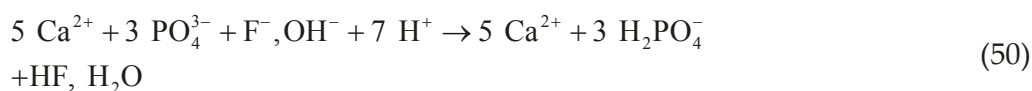
4. **Congruent and incongruent dissolution model:** was already described above.
5. **Chemical model:** This model was developed from the self-evident supposition that it would be highly unlikely if apatite were dissolved by the detachment of "single molecules" equal to the unit cells and consisting of 18 ions. Moreover, in the crystal lattice, practically all ions are shared with neighboring unit cells and often cannot be attributed to given "single molecule." Based on the experimental results obtained on one hand, and on analysis of the data found in references on the other hand, a sequence of four successive chemical reactions was proposed to describe the process of apatite dissolution [112], [187],[212],[213]:



Eqs. 44–47 can be used instead well-known net reactions [187]:



In principle, the dissolution process could also happen according to reaction 49 followed by chemical interaction in the solution among ions of apatite and acid near the crystal surface [214]:



1. **Etch pit formation:** the process of etch pit formation describes the dissolution of apatite crystals containing structural defects (dislocations and inclusions). The presence of dislocations accelerates the dissolution because they give rise to continuous steps on the surface and the strain energy, which they cause in crystals, favors the etch pit formation. The pits appear at the dislocation outlets; they are 0.1–10 µm in size (the dimensions depend on the dissolution kinetics and dissolution time: they increase when the dissolution progresses) and usually have a hexagonal shape according to the crystal symmetry $\text{P6}_3/\text{M}$ of pure apatite [187],[215],[216],[217],[218],[219].
2. **Ion exchange model:** based on a supposition about the adsorption of protons and anions of acid (e.g. citrate anions) from a solution onto the surface of apatite and removing of ions of calcium and phosphate into the solution instead [187].
3. **Hydrogen catalytic model:** based on a reasonable suggestion about the adsorption of protons onto negatively charged oxygen ions of phosphate groups of apatite. The sorption of protons results in the transformation of surface PO_4^{3-} groups into HPO_4^{2-} and catalyzes the dissolution process [187].

3.4.3 Methods for the evaluation of reactivity of phosphate rocks

Chemical methods are used for the evaluation of reactivity of different phosphate rocks from which the fertilizers are manufactured for their possible direct application as fertilizers via empirical solubility test. Citric acid, formic acid, neutral ammonium citrate,³⁸ and alkaline ammonium citrate are used as solvents for the extraction of P_2O_5 . The latter is used mainly for the evaluation of calcined aluminum phosphates. Most of these reagents were not originally intended to evaluate the reactivity of phosphate rocks. For instance, neutral and alkaline ammonium citrate solutions were originally intended to separate chemical reaction products in superphosphate and other fertilizers from unreacted rock on the assumption that unreacted rock was insoluble in these reagents. The citric acid extraction was developed to evaluate basic slag, a popular fertilizer material in European countries. The formic acid extraction was developed specifically for phosphate rocks [220].

Nearly all extraction methods use the ratio of sample weight to extraction volume 1 g:100 ml.

³⁹ The extraction time usually ranges from 30 min to 1 hour. The temperature and the agitation during extraction test may be specified. For example, the AOAC method uses neutral ammonium citrate⁴⁰ of specified concentration (1 g of sample and 100 ml of solution) with the extraction time of 30 min at 65°C. The Wagner method uses 2% solution of citric acid, the

³⁸ Neutral ammonium citrate is prepared by dissolving required amount of citric acid and neutralizing it with ammonium hydroxide. The pH of the reagent is adjusted to neutral [221].

³⁹ The amount of used solution is also expressed in the name of the method, e.g. 100 ml method or 150 ml method [222].

⁴⁰ The neutral ammonium citrate test was used as the official method in the United States, and the test by acidic acid was developed for the comparison [222].

extraction time of 30 min and the temperature of 17.5°C [220],[221],[222],[223]. Unavailable phosphoric acid is usually expressed as the portion of fertilizer, which is *insoluble* in neutral ammonium citrate [769]. Phosphate removed during the neutral ammonium test is termed as *citrate-soluble*. The sum of *water-soluble* and *citrate-soluble* phosphate is termed as *available* [224].

Fused magnesium phosphate (FMP) is highly soluble in 2% citric acid⁴¹ but is less soluble in neutral citrate, while calcined defluorinated phosphate (CDP) and Thomas slag (Thomas phosphate) are fairly soluble in both citric acid and citrate. Actually, FMP dissolves fairly rapidly in neutral citrate at the beginning, but the dissolution is hindered by gelatinous silica, which forms on the surface of the FMP particles. This layer can be broken by vigorous stirring [222].

One disadvantage of all these methods is that the percentage of leached P₂O₅ depends on the grade of the rock, especially when the rock contains inert gangue minerals such as silica. In order to eliminate the adventitious effect of grade, the concept of absolute citrate solubility index (ASC) was developed [225],[226]:

$$ASC = \frac{\text{AOAC citrate solubility P}_2\text{O}_5 [\%]}{\text{Theoretical P}_2\text{O}_5 \text{ in apatite } [\%]} \quad (51)$$

The percentage of dissolved P₂O₅ is expressed as the gangue-free apatite [220]. If rocks contain free calcium or magnesium carbonate, these carbonates should be removed by the extraction with a suitable reagent before carrying out the test in order to obtain correct indication of reactivity [227].

It was also found that the length of the *a*-axis in the apatite unit cell (*a*₀) is statistically related to the ASC according to the relationship [225]:

$$ASC = 421.4 (9.369 - a_0) \quad (52)$$

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⁴¹ It is believed that weak citric acid solution imitates the condition near the plant roots [222].

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