

## 2. IRON IN THE UNIVERSE

Iron is a relatively abundant element in the Universe (Lide, 2004). In the Universe there are two main kinds of stars, those of low-mass and high-mass (Bennett *et al.*, 2004). The low-mass stars could exist for billions of years, but only high-mass stars (exceeding in 8 times of Sun's mass), whose life could be relatively short, produce heavy elements. In fact, all elements heavier than lithium were produced by stars (Bennett *et al.*, 2004). The centres of high-mass stars are capable of reaching much higher temperatures than in low-mass stars, and thus they can fuse much heavier elements. So, massive stars go through several nuclear burning stages beyond helium fusion, creating new, heavier elements at each stage, until fusion reactions form iron. During the evolution of high-mass stars, an iron core is formed by collecting iron generated in fusion reactions. The core would continue heating, and growing in mass, as light elements fuse into heavier elements, with the accumulation of iron formed by such fusion. The formation of elements even heavier than iron would take place if iron itself were to participate in fusion reactions. However, iron is a unique element, which, among all elements, has the minimal average mass per nuclear particle (see, for example, Figure 17.20 in Bennett *et al.*, 2004). Iron is the heaviest element that can be created through a fusion process in which energy is released. This means that elements lighter than iron could generate energy in fusion reactions and elements heavier than iron could generate energy in fission reactions; however, iron itself would generate no amount of energy either as a component of a fusion, or a fission reaction. Therefore, iron cannot participate in these reactions; which leads to the accumulation of iron in the star's core, causing it to grow indefinitely. This property of iron is used in one of the most credible hypotheses on the formation of a supernova (discussed in details in Bennett *et al.*, 2004). The hypothesis is based on such facts as the abovementioned property of iron of having minimal average mass per nuclear particle, limited distance between electrons allowed by quantum mechanics, and the reduction of size of atom under increase of pressure. As soon as the matter in a stellar core turns to iron, it can generate no further thermal energy or pressure. At the same time, the growing gravity pressure could push electron shells too close to each other and to the atomic nuclei, which could lead to the combining of electrons with protons to form neutrons. In an instant, the iron core would be converted to neutrons, creating a giant

empty space. Such gravitational instability could cause a very quick collapse of the layers of the star with an instant release of a colossal amount of energy, generating a supernova. The exploding star would release a gigantic quantity of matter into the galaxy. This means that chemical elements up to iron on the Periodic Table are produced by fusion reactions in the cores of massive stars, but elements heavier than iron are produced during brief fusion reactions that occur during a supernova explosion.

Our Sun is a low-mass star, and cannot generate all chemical elements. Moreover, the Sun was formed from the same nebula that were all the planets and moons of the solar system, meaning that the matter of the nebula existed prior to the beginning of the formation of solar system. Consequently, material of solar and other nebulas in the galaxy was produced by stars of a previous generation, which had likely undergone a supernova explosion, and the matter comprising these nebulas was recycled into the new generation of stars.

Our knowledge about iron content in the Universe is mostly related to known facts and observations of the solar system and some theoretical researches. Within the solar system, significant concentrations of iron were found in meteorites, rocks of terrestrial planets, and are expected in the cores of terrestrial planets and some moons of Jupiter. Furthermore, iron vapor was defined in the Sun's atmosphere (Anderson, 1990; Kaufmann and Freedman, 1999). The abundance of main chemical elements, including iron, for the Sun, Earth, meteorites and "Cosmic" matter are presented in Table 2.1, based on generalization of some investigations (McCall, 1973; Anders and Ebihara, 1982; Clark, 1982; Porterfield, 1984; Breneman and Stone, 1985; Anderson, 1990; Cox, 1990). In addition to Table 2.1, in Table 2.2 element abundances in the Universe, Sun, chondrites, iron meteorites, stony meteorites, and Earth crust are presented.

It should be taken into account that the most abundant elements within the Sun and correspondingly in the solar system are hydrogen and helium, which are not among the most abundant elements in the Earth and other terrestrial planets. It is evident from the data shown in Tables 2.1 and 2.2 that iron is one of the most abundant elements in the Universe, but for Earth, iron is the most abundant element. More detailed information about the iron content of meteorites,

Table 2.1

Abundances of main chemical elements

| Element | Elemental abundances, ppm |                   |        |                           |                                |                              |            |          |
|---------|---------------------------|-------------------|--------|---------------------------|--------------------------------|------------------------------|------------|----------|
|         | Earth, whole              | Continental crust | Ocean  | Sun's corona <sup>a</sup> | Sun's photosphere <sup>a</sup> | "Cosmic" matter <sup>a</sup> | Meteorites | Universe |
| O       | 295121                    | 467735            | 6***   | 5680                      | 22900                          | 20100                        | 346000     | 10700    |
| Mg      | 151356                    | 32359             | 1270   | 1089                      | 1089                           | 1075                         | 139000     | 580      |
| Al      | 14791                     | 83176             | 0.001  | 83.7                      | 83.7                           | 84.9                         | 14000      | 55       |
| Si      | 144544                    | 269153            | 3      | 1000                      | 1000                           | 1000                         | 178000     | 650      |
| S       | 43652                     | 631               | 2650** | 242                       | 460                            | 515                          | 20000      | 440      |
| Ca      | 16982                     | 52481             | 400    | 82                        | 82                             | 61.1                         | 16000      | 67       |
| Fe      | 301995                    | 69183             | 0.007  | 1270                      | 1270                           | 900                          | 256000     | 1090     |
| Ni      | 16218                     | 100               | 0.0066 | 46.5                      | 46.5                           | 49.3                         | 14000      | 60       |

\* - quotes for word "Cosmic" are used by Anderson, 1990

\*\* - concentration as (SO<sub>4</sub>)<sub>2</sub>

\*\*\* - oxygen dissolved in ocean water (oxygen content ~ 89%)

a - abundances in atoms/1000 Si atoms

Table 2.2

Abundances of main chemical elements (compiled using data of Clark, 1982)

| Element | Elemental abundances                     |                                     |                      |                    |                     |                        |                       |
|---------|--|-------------------------------------|----------------------|--------------------|---------------------|------------------------|-----------------------|
|         | Universe, atoms/10 <sup>6</sup> Si atoms | Sun, atoms/10 <sup>6</sup> Si atoms | Chondrites, ppm      | Iron meteorites, % | Stony meteorites, % | Continental crust, ppm | Crust as a whole, ppm |
| O       | 2.15-2.90·10 <sup>7</sup>                | 2.90·10 <sup>7</sup>                | 3.5·10 <sup>5</sup>  | –                  | 35.71               | 4.61·10 <sup>5</sup>   | 4.56·10 <sup>5</sup>  |
| Mg      | 0.91-1.05·10 <sup>6</sup>                | 7.90·10 <sup>5</sup>                | 1.40·10 <sup>5</sup> | –                  | 13.67               | 2.33·10 <sup>4</sup>   | 2.76·10 <sup>4</sup>  |
| Al      | 8.90-9.50·10 <sup>4</sup>                | 5.00·10 <sup>4</sup>                | 1.30·10 <sup>4</sup> | –                  | 1.52                | 8.23·10 <sup>4</sup>   | 8.36·10 <sup>4</sup>  |
| Si      | 1.00·10 <sup>6</sup>                     | 1.00·10 <sup>6</sup>                | 1.80·10 <sup>5</sup> | –                  | 18.07               | 2.81·10 <sup>5</sup>   | 2.73·10 <sup>5</sup>  |
| S       | 3.75-6.00·10 <sup>5</sup>                | 0.63-1.08·10 <sup>6</sup>           | 2.00·10 <sup>4</sup> | 0.08               | 1.8                 | 350                    | 340                   |
| Ca      | 4.90-7.28·10 <sup>4</sup>                | 4.50·10 <sup>4</sup>                | 4.50·10 <sup>4</sup> | –                  | 1.73                | 4.15·10 <sup>4</sup>   | 4.66·10 <sup>4</sup>  |
| Fe      | 0.85-6.00·10 <sup>4</sup>                | 1.17·10 <sup>5</sup>                | 2.50·10 <sup>5</sup> | 89.70              | 23.31               | 5.63·10 <sup>4</sup>   | 6.22·10 <sup>4</sup>  |
| Ni      | 1.5-2.74·10 <sup>4</sup>                 | 2.6·10 <sup>4</sup>                 | 2.48·10 <sup>4</sup> | 9.10               | 1.53                | 84                     | 99                    |

combined using published data (McCall, 1973; Kaler, 1994; McSween, 1999), is generalized in Table 2.3.

The following table (Table 2.4) displays Fe-Ni-metal content and types of Fe-containing minerals in main kinds of meteorites. Table 2.4 was composed using data of Mason (1962), McCall (1973), Buchwald (1976), Anderson (1990), Kaler (1994), Norton (1994), Norton and Norton (1998), McSween (1999), Grady (2000), Krot *et al.* (2002), Bradley (2003), Brearley (2005), Scott and Krot (2005a, 2005b, 2005c), and Righter *et al.* (2006). The analysis of different types and groups of meteorites presented in Table 2.4 indicates that all referenced types of meteorites contain metallic iron, along with a significant content of iron

in silicates. Among achondrites, only ureilites contain a significant amount of metallic iron, and in other types of achondrites metal phases (Fe, Ni) are near absent. Carbonaceous chondrites are primitive and undifferentiated meteorites that formed in oxygen-rich regions of the early solar system, and some of their groups show a high content of water (CI chondrites contain up to 20% of water). Most of the iron is not presented in its pure form but is found in silicates, oxides, or sulfides.

Analysis of average iron content of a silicate phase gave for FeO+Fe<sub>2</sub>O<sub>3</sub> content in chondrites and achondrites values of ~15.4 mass% and ~11.45 mass%, respectively (Clark, 1982). Very high content of iron

**Table 2.3**

Iron content of meteorites

| Type of meteorite       | Frequency, % | Content of iron                                    |
|-------------------------|--------------|--|
| Carbonaceous chondrites | 5            | Magnetite and some fayalite (Fa <sub>32-40</sub> ) |
| Chondrites              | 81           | 10.58% of Ni-Fe; 42.31% olivine, 28.91% pyroxenes  |
| Achondrites             | 8            | 1.57% of Ni-Fe, 12.82% olivine, 62.25% pyroxenes   |
| Stony irons             | 1            | 50% free metal and Fa olivine up to 21 %           |
| Irons                   | 5            | 90% iron   |

in chondrules (Wood, 1962; Righter *et al.*, 2006) could be explained by the significant reduction of the melting point of iron-containing silicates, compared to magnesium-containing silicates (Kushiro *et al.*, 1968; McCall, 1973; Pilchin and Eppelbaum, 2004,2005). Meteorites of the CK group contain a high percentage of magnetite that is dispersed in a matrix consisting of iron-rich olivine and pyroxene. For meteorites of the CO group, the presence of small, clearly visible inclusions of free metal (mostly nickel-iron) is characteristic. In meteorites of the CR group, free metal and iron sulfide are found in both the matrix and chondrules, and sometimes chondrules are embedded into small rims of nickel-iron or iron sulfide. The matrix of CV chondrites mainly consists of iron-rich olivine. In H chondrites, the matrix displays abundant iron flakes and facets, which are often oxidized; while the matrix of LL chondrites displays very little visible iron. Almost all the iron in E chondrites is visible as free metal. Pallasites consist of olivine crystals embedded in a Fe-Ni alloy matrix. The metal phase in mesosiderites, however, does not form a continuous matrix of free metal, and they usually display a mixture between the silicate and metal phases.

As noted McCall (1973), most meteorites contain FeO and only a few of them contain Fe<sub>2</sub>O<sub>3</sub>. Most of researchers believe that the Earth, as well as other terrestrial planets and some moons of Jupiter, have a metallic, mostly iron core. However, a comparison of the iron content of meteorites with the iron content of different rocks representing different levels within the Earth shows that the content of iron in terrestrial planets is significant. Iron content of different parts of the Earth (using data of Anderson, 1980, 1990, 1999; Jacobsen *et al.*, 1984; Maaløe and Steel, 1980; Morgan and Anders, 1980; Ringwood and Kesson, 1976; and Ganapathy and Anders, 1974), other terrestrial planets, and the Moon (using data of Anderson, 1972a, 1980,

1990; Basaltic-BVP project, 1980) are compiled in Tables 2.5 and 2.6.

Data presented in Tables 2.5 and 2.6 illustrate that the iron content of terrestrial planets is very high. Iron composes more than half of the mass of Mercury, and approximately one third of the mass of Earth. Iron also composes more than a quarter of the mass of Venus and Mars. Analysis of estimations of iron content made for terrestrial planets by different authors using different models shows (Anderson, 1990) that the average content of FeO in the mantle and crust is 0-3.7% for Mercury, 0.24-5.4 % for Venus, 7.9-8.9% for Earth, 15.8-24.3% for Mars, and 13% for the Moon. A similar analysis of estimations of the Fe content of the cores of terrestrial planets (Anderson, 1990) gave values of 93.5-94.5% for Mercury, 84.7-94.4% for Venus, 89.2% for Earth, and 59.8-88.1% for Mars. The small amount of FeO in the mantle of Mercury is also supported by spectroscopic measurements (Solomon, 2003) and other data (Righter *et al.*, 2006). At the same time, the mantle FeO content of Mars being highest among terrestrial planets is supported by numerous researches (Longhi *et al.*, 1992). A small core size (~10-20%) and high mantle FeO content (~25 wt.%) were also estimated for asteroid 4 Vesta (Righter and Drake, 1997). Palme (2004) estimates that the bulk iron content of the Moon is in range of 8 to 12%, compared to 31% for Earth. High iron content of the Moon's crust and mantle (see Table 2.6) is consistent with data showing that lunar basalts are richer in iron oxide than their terrestrial counterparts (Palme, 2004). Clark (1982) noted that content of FeO+Fe<sub>2</sub>O<sub>3</sub> in basaltic lunar rocks is in the range of 7.78-26.75 % with an average value of ~19%. Hood (1986) estimated the size of the Moon's core at about 2-4% of its mass. This data, along with the data from Tables 2.5 and 2.6 shows that there are clear trends of an increasing iron content in the crust and mantle of terrestrial planets with the

**Table 2.4**

Content of metallic iron (as Fe, Ni) and iron containing minerals in some meteorites

| Group                          | Type | Fe,Ni metal (vol. %) | Iron containing minerals  |
|--------------------------------|------|----------------------|---|
| <b>Carbonaceous chondrites</b> |      |                      |   |
| CI                             | 1    | < 0.01               | ferrhydrite, magnetite, pyrrhotite  |
| CM                             | 1-2  | 0.1                  | pyrrhotite, magnetite   |
| CO                             | 3    | 1-5                  | Fe-Ni metal, sulfides, Fe-silicates, magnetite, Fe-rich olivine, ferric oxide |
| CV                             | 2-3  | 0-5                  | Fe-rich olivine, low-Ni metal, FeS, magnetite                                 |
| CK                             | 3-6  | < 0.01               | Fe-rich olivine, magnetite, augite, sulfides                                  |
| CR                             | 1-2  | 5-10                 | Fe-Ni metal, magnetite, FeS, pyrrhotite                                       |
| CH                             | 3    | Up to 15-20          | Fe-Ni metal, Fe-rich olivine  |
| CB                             | 3    | 50-70                | Fe-Ni metal   |
| <b>Ordinary chondrites</b>     |      |                      |   |
| H                              | 3-6  | 8 - 21               | Fe-Ni metal, Fe-rich olivine, sulfides  |
| L                              | 3-6  | 3-10                 | Fe-Ni metal, Fe-rich olivine, sulfides, hypersthene                           |
| LL                             | 3-6  | 1.5-2                | Fe-rich olivine, magnetite, Fe-Ni metal, hypersthene                          |
| <b>Enstatite chondrites</b>    |      |                      |   |
| EH                             | 3-6  | 8                    | Fe-Ni metal, sulfides   |
| EL                             | 3-6  | 15                   | Fe-Ni metal, sulfides   |
| <b>Other chondrites</b>        |      |                      |   |
| K                              | 3    | 6-9                  | troilite, Fe-Ni metal, ferrhydrite  |
| R                              | 3-6  | <0.1                 | Sulfide   |
| <b>Bronzite chondrites</b>     |      |                      | Fe-rich olivine – Fa <sub>15-22</sub>   |
| <b>Hypersthene chondrites</b>  |      |                      | Fe-rich olivine – Fa <sub>22-32</sub>   |
| <b>Achondrites ureilites</b>   |      | Up to 5              | Fe-Ni metal   |
| <b>Irons</b>                   |      |                      |   |
| Hexahedrites                   |      | Up to 100*           | Kamacite  |
| Octahedrites                   |      | Up to 100*           | Kamacite, taenite   |
| Ataxites                       |      | Up to 100*           | Taenite, kamacite   |
| <b>Stony irons</b>             |      |                      |   |
| pallasites                     |      | Up to 50*            | Fe-Ni metal, Fe-rich olivine  |
| Mesosiderites                  |      | Up to 50*            | Fe-Ni metal, Fe-rich olivine, troilite  |
| Lodranites                     |      | Up to 35-50*         | Fe-Ni metal, Fe-rich olivine  |

\* - in wt. %

**Table 2.5**

Earth's interior structure and iron content

| Region            | Depth, km | Percent of Earth's mass | Iron content, % |
|-------------------|-----------|-------------------------|-----------------|
| Continental crust | 0-50      | 0.374                   | 5.83-7.10*      |
| Oceanic crust     | 0-10      | 0.099                   | 8.16            |
| Mantle            | 10-2890   | 67.2-67.4               | 5.3-6.94*       |
| Core              | 2890-6370 | 32.3-32.5               | 89.2            |
| Total             | 0-6370    | ≈100                    | 32.52-33.68*    |

\* - calculations made using a few different models

increase of their distance from the Sun, while the core size of terrestrial planets increases with proximity to the Sun. These facts attest to the dependence of the composition of terrestrial planets on heliocentric distance (Righter *et al.*, 2006). The abovementioned facts of iron content in the cores and mantles of terrestrial planets are in agreement with the presence of iron in meteorites and terrestrial planets as a pure metal (Fe), iron oxides (FeO and Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). Really, all these minerals have different densities (Table 2.7), and as a result of which could be differently attracted by the forming Sun.

Analysis of iron content in meteorites (see Table 2.4) indicates that they contain metallic iron, FeO in

**Table 2.6**

Iron content of terrestrial planets and Moon

| Region           | Mercury         |                 | Venus           |                 | Mars            |                 | Moon            |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | Percent of mass | Iron content, % | Percent of mass | Iron content, % | Percent of mass | Iron content, % | Iron content, % |
| Mantle and crust | 33              | 0               | 69.1            | 1.64            | 88.1            | 18.95           | 10.14           |
| Core             | 67              | 94.5            | 30.9            | 87.00           | 11.9            | 72.00           |                 |
| Total            | 100             | 63.32           | 100             | 28.02           | 100             | 25.26           |                 |

**Table 2.7**

Average density of iron, iron oxides, magnetite, and some other iron containing minerals

| Mineral   | Density, kg/m <sup>3</sup> |
|---|----------------------------|
| Iron, Fe  | 7870                       |
| Ferrous iron oxide, FeO   | 5880                       |
| Ferric oxide, Fe <sub>2</sub> O <sub>3</sub>                                | 5300                       |
| Magnetite, Fe <sub>3</sub> O <sub>4</sub>                                   | 5150                       |
| Pyrite, FeSi <sub>2</sub>   | 5010                       |
| Troilite, FeS   | 4610                       |
| Pyrrhotite, FeS   | 4610                       |
| Fayalite, Fe <sub>2</sub> SiO <sub>4</sub>                                  | 4390                       |
| Almandine, Fe <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> | 4190                       |
| Ferrosilite, FeMgSi <sub>2</sub> O <sub>6</sub>                             | 3950                       |

silicates, magnetite and iron sulfides, but ferric iron oxide (Fe<sub>2</sub>O<sub>3</sub>) is usually not present. It should also be taken into consideration that fayalite is usually found as a solid solution with less dense forsterite, and dense almandine is usually present in solid solutions with less dense pyrope and grossular. This means that within the solar nebula the highest gravity attraction was applied to metallic iron, and the value of this attraction was reducing with the decrease of density of iron-containing compounds. This possibly led to a higher concentration of metallic iron and a lower concentration of magnetite, and iron-containing sulfides and silicates at the distance at which Mercury is from the Sun. At the same time, intermediate concentrations of metallic iron, magnetite and iron-containing sulfides and silicates were at the distance at which Venus and Earth are from the Sun; and a low content of metallic iron with a high content of magnetite and iron-containing sulfides and silicates was at the distance at which Mars is from Sun. This is also consistent with the much higher average density of Mercury, Venus and Earth, compared to the average density of Mars (Table 2.8).

**Table 2.8**

Average density of terrestrial planets

| Planet  | Average density, kg/m <sup>3</sup> |
|---------|------------------------------------|
| Mercury | 5430                               |
| Venus   | 5240                               |
| Earth   | 5520                               |
| Mars    | 3930                               |

Such a distribution of iron-containing compounds could explain the high content of metallic iron with negligible content of iron-containing sulfides and silicates within Mercury. It also explains the high content of iron-containing silicates and low content of metallic iron within Mars.

Additional support to this hypothesis could come from the total weight of the content of iron in the Sun and terrestrial planets (Table 2.9). Data of Table 2.9 indicate that even though the relative content of iron in the Sun is extremely low, its value by total mass (in kg) is about 100 times greater than that of all terrestrial planets together.

Some geothermal data show that at the time of core formation, Earth (and possibly Venus and Mars) may have been entirely molten (Jakosky, 1999; Walter and Trønnes, 2004). Under such conditions, any free iron would be heavy enough to sink through the molten rock.

Since the Sun contains the majority of the mass in the solar system and the main components of the Sun are hydrogen and helium, it is clear that these two elements are by far the most abundant elements in the solar system (~98% of the solar nebula: Bennett *et al.*,

**Table 2.9**

Content of iron in Sun and terrestrial planets

| Name    | Mass, kg              | Iron content |                              |
|---------|-----------------------|--------------|------------------------------|
|         |                       | wt %         | kg                           |
| Sun     | $1.99 \times 10^{30}$ | 0.1792       | $3.566 \times 10^{26}$       |
| Mercury | $3.30 \times 10^{23}$ | 63.32        | $2.09 \times 10^{23}$        |
| Venus   | $4.87 \times 10^{24}$ | 28.02        | $1.36 \times 10^{24}$        |
| Earth   | $5.97 \times 10^{24}$ | 31.00-33.68  | $(1.85-2.01) \times 10^{24}$ |
| Mars    | $6.42 \times 10^{23}$ | 25.26        | $1.62 \times 10^{23}$        |

2004). However, Tables 2.1-2.6 illustrate that even though the initial content of metals in the solar nebula was ~0.2% of its mass (Bennett *et al.*, 2004), their presence was crucial for the composition, structure and possibly existence of terrestrial planets and some moons in the solar system. The concentration of metals in terrestrial planets is much higher than that of other planets in the solar system; and in the cases of Earth and Mercury, iron is the most abundant element. Even though Mars has the highest iron content of crust and mantle, its planetary density is the lowest among the terrestrial planets. High iron content of Martian rocks can also be demonstrated by the high content of a reddish-orange dust covering the Martian surface and filling its craters. Furthermore, that Mercury has the second highest density among the planets of the solar system could be explained by its high iron content (Table 2.6).

### 3. IRON AS A MARKER OF SPECIFIC CONDITIONS DURING EARTH EVOLUTION

Even though oxygen is the most abundant element of the Earth crust and the second most abundant element of total Earth content, most researchers believe that during a significant period of time Earth's atmosphere was essentially anoxic (Kasting and Donahue, 1980; Holland, 1984; Kasting, 1987; Wiggering and Beukes, 1990; Eriksson and Cheney, 1992; Rye and Holland, 1998; Knoll, 2003, etc.), and that until the Early Proterozoic its oxygen content was below  $10^{-5}$  of the present oxygen level. This is based on the assumption that some processes and features could take place exclusively in an anoxic environment. This means that some processes could be employed as indicators of specific conditions at different points in time in the evolution of Earth. For example, such processes as the deposition of banded iron formations (BIFs), oxidation

of iron from its ferrous to ferric state, formation of paleosols, formation of red beds, duration of pyrite formation, and some other processes are usually correlated to the time of transfer from anoxic to oxic atmosphere environments (Kasting and Donahue, 1980; Gay and Grandstaff, 1980; Holland, 1984; Grandstaff *et al.*, 1986; Retallack, 1986; Kasting, 1987; Wiggering and Beukes, 1990; Eriksson and Cheney, 1992; Macfarlane *et al.*, 1994; Ohmoto, 1996; Rye and Holland, 1998; Knoll, 2003; Utsunomiya *et al.*, 2003, etc.).

Researches usually account the deposition of BIFs, pyrite deposits, and deposits of uraninite among the processes which could be developed exclusively in anoxic atmosphere environments. These processes could therefore be considered markers of anoxic environments, and most importantly an essentially anoxic atmosphere with an oxygen pressure of less than  $10^{-5}$  of the present oxygen pressure. At the same time, many investigators consider the start of the formation of such deposits as red beds and paleosols as a marker of the atmosphere transitioning from an anoxic to an oxic state (Kasting and Donahue, 1980; Holland, 1984; Kasting, 1987; Wiggering and Beukes, 1990; Eriksson and Cheney, 1992; Rye and Holland, 1998; Knoll, 2003, etc).

Most researchers believe that iron oxides and silica, the main components of BIFs, were deposited from seawater (Cloud, 1973; Holland, 1984; Young, 1988; Huston and Logan, 2004; Kopp *et al.*, 2005, etc.). Some researchers believe that the presence of BIFs indicates that iron initially occurred in its reduced state Iron(II), and only turned to its oxidized Iron(III) form with rising oxygen levels in the atmosphere (Kasting and Donahue, 1981; Holland, 1984; Klein and Beukes, 1992; Kasting, 1993; etc.). This is based on the theory that reduced iron is much more soluble than oxidized Iron(III). So, the emergence of BIFs shows that the concentration of oxygen in the atmosphere and early oceans was not enough to convert all Iron(II) to Iron(III)-oxide. As soon as a sufficient amount of oxygen enters the atmosphere, iron takes the oxidized state Iron(III) and is no longer soluble. This leads to the formation of paleosols and red beds containing mostly ferric iron. The first occurrence of red beds marks this major atmospheric transition in Earth's evolution. However, a recent investigation (Hamade' *et al.*, 2003) suggests a continental component in the silica flux of BIFs. Other authors (Krapez *et al.*, 2003),

accomplished research for the Early Palaeoproterozoic BIF in the Brockman Supersequence of Western Australia, and came to the conclusion that this BIF was not formed by the high-frequency alternating precipitation from ambient seawater containing iron minerals and silica.

BIFs were deposited mostly in greenstone belts throughout the duration of a significant span of time, starting as early as 3.85 Ga in Greenland (Klein, 2005) and 3.5 Ga in Australia (Klein, 2005), and ending around 1.80-1.85 Ga (Klein and Beukes, 1992; Kasting, 1993; Huston and Logan, 2004; Klein, 2005). BIFs are usually classified as either Algoma- or Superior-type (Gross, 1983; James, 1983; Gross, 1996a, 1996b; Huston and Logan, 2004; Klein, 2005). Analysis of the distribution of BIFs through time shows (Huston and Logan, 2004) that the main periods of BIFs deposition were about 3.3-3.1 Ga (greatest amount of BIFs) and 2.8-2.7 (greatest number of BIFs) for Algoma-type, and about 2.6-2.4 (greatest by amount of BIFs) and 2.1-1.8 (greatest by number of BIFs) for Superior-type BIFs. James (1983) accounted the early Proterozoic period of BIFs deposition as a single period from 2.5 Ga to 1.9 Ga, and deposits of this period were estimated as 90% of all iron formations.

Numerous authors used chemical profiles of paleosols for the reconstruction of the atmospheric oxygen level during early Earth evolution (Holland, 1984; Wiggering and Beukes, 1990; Eriksson and Cheney, 1992; Rye and Holland, 1998; Utsunomiya *et al.*, 2003, etc.). Paleosols are the ancient weathering profiles formed by chemical means with very specific conditions of water-rock-atmosphere interaction (Rye and Holland, 1998). One of the most important facts of paleosols weathering is the mobility of iron. All known paleosols lost iron from their upper parts during weathering (Holland, 1984; Rye and Holland, 1998; Utsunomiya *et al.*, 2003, etc.). The idea of iron mobility is based on the known facts that Iron(II) is soluble in water and Iron(III) is insoluble in water, and that iron is the dominant element that consumes oxygen during the weathering of igneous rocks (Rye and Holland, 1998; Utsunomiya *et al.*, 2003). This means that if there was enough oxygen in the atmosphere, Iron(II) would have oxidized to Iron(III) during weathering and iron within paleosol would not be soluble and mobile. This means that paleosols could provide valuable information about the concentration of oxygen in the atmosphere during their formation.

“Definite paleosols” analysed by Rye and Holland (1998) are of the Late Archean, Early Proterozoic, Grenvillian and Paleozoic age; and among “likely paleosols”, they found mostly ages of the Late Archean and low Early Proterozoic. Other researches also show ages of the Archean (Grandstaff *et al.*, 1986; Retallack, 1986; Macfarlane *et al.*, 1994), low Early Proterozoic (Gay and Grandstaff, 1980; Ohmoto, 1996; Utsunomiya *et al.*, 2003), middle Early Proterozoic (Wiggering and Beukes, 1990), Grenvillian (Zbinden *et al.*, 1988), Mesozoic (Sheldon and Retallack, 2002) and Cainozoic (Kleinert and Strecker, 2001) for paleosols.

Rye and Holland (1998) indicate that out of 50 investigated paleosols 48 were older than 1.7 Ga, Pre-2.44 Ga paleosols suffered significant iron loss during weathering, and in some cases Hakkalampi (2.44-2.2 Ga), Ville Marie (2.38-2.215 Ga) and Hekpoort (2.245-2.203 Ga) paleosols were immediately overlain by Red beds. At the same time, iron loss was negligible during the formation of the 2.2-2.0 Ga Wolhaarkop and Drakenstein and all later paleosols reviewed (Rye and Holland, 1998). This is consistent with results showing that paleosols developed before 2.4 Ga show substantial iron loss, whereas younger paleosols retain weathered iron (Beukes *et al.*, 2002).

Another feature related to the presence of iron in sedimentary layers is the formation of red beds. Red beds are detrital sedimentary rocks rich in reddish-brown ferric oxide, which is why some researchers believe that the appearance of red beds is an indicator of oxygen buildup in the atmosphere. There is a controversy in pinpointing the time of the emergence of red beds as well. Some authors believe that redbeds, oxidized subaerial deposits, were absent prior to about 2 Ga (Kasting, 1993). Other authors are referencing 2.2 Ga (Nisbet and Sleep, 2001) as the time of the first appearance of red beds. Various researches show that red beds were formed in the beginning of Early Proterozoic (Aspler and Chiarenzelli, 1997), middle of Early Proterozoic (Wiggering and Beukes, 1990; Eriksson and Cheney, 1992; Aspler and Chiarenzelli, 1997), end of Early Proterozoic (Eriksson and Cheney, 1992; Eriksson *et al.*, 1997), Middle Proterozoic (Eriksson and Vos, 1979; Eriksson *et al.*, 1997; Rainbird *et al.*, 2003), Late Proterozoic (Knoll *et al.*, 1995), Early Paleozoic (Huang *et al.*, 2000), and Mesozoic (Dong *et al.*, 2004).

Such wide dispersion of all those rock formations through time, and the obvious overlapping of processes

of the formation of BIFs with the processes of the formation of paleosols and red beds, does not allow for an unambiguous definition of any specific point in time that could be accepted as a transition between anoxic and oxic atmospheres.

Unfortunately, none of the abovementioned authors took into consideration the results of thermodynamic researches on the problem of iron oxides stability (this problem will be discussed in Chapter 5). Moreover, some researches do not support the statement that ferrous iron compounds are soluble and ferric iron compounds are not soluble (Clark, 1982; Porterfield, 1984; Lide, 2004). Solubility of some iron-containing chemical compounds is presented in Table 3.1.

The data of Table 3.1 do not fully support the opinion of some scientists (for example, Cox, 1990; Rye and Holland, 1998, etc.) that the formation of paleosols and red beds is related to the fact that compounds of ferrous iron ( $Fe^{2+}$ ) are more soluble than compounds of ferric iron ( $Fe^{3+}$ ). The data show (Table 3.1) that both ferrous iron and ferric iron compounds are found in both low-soluble and high-soluble compounds (Lide, 2004); and such soluble compounds as  $FeCl_3$ ,  $Fe_2(SO_4)_3$  of Iron(III) are even more soluble than similar compounds  $FeCl_2$ ,  $FeSO_4$  of Iron(II) (Lide, 2004). Both  $Fe(OH)_2$  and  $Fe(OH)_3$  are extremely low-soluble, with a solubility of much less than that of numerous known low-soluble compounds, for example carbonates and barite (Lide, 2004), while  $Fe(OH)_2$  is unstable in the presence of air (Akhmetov, 1992; Benali *et al.*, 2001). This means that difference in solubility cannot be the only cause of the formation of paleosols and red beds. Furthermore, all iron compounds integral to the deposition of BIFs ( $FeCO_3$ ,  $Fe(OH)_2$ ,  $Fe(OH)_3$ , as well as iron oxides themselves) are insoluble and cannot be part of "iron-rich ocean water", as proposed by some authors (Young, 1988; Kopp *et al.*, 2005) to explain the deposition of BIFs. Moreover, researches show that the concentration of iron in fresh and seawater (see Table 3.2) cannot explain the deposition of BIFs from seawater.

In reality, the concentration of iron in seawater is so low (Table 3.2) that it cannot explain its low-soluble compounds even if all the iron dissolved in seawater were to represent the giant deposits of BIFs in ocean environments. The data in Table 3.2 indicate that the formation of some iron deposits is more likely to take place from freshwater, in which the quantity of dissolved iron is dozens or even hundreds of times

greater than its concentration in seawater. Excess iron could also be deposited from fresh water in the area of its contact with seawater. This means that if iron deposits were formed in the presence of water, they were most likely formed in the continental areas.

At the same time, such low concentrations of iron in both seawater and freshwater cannot support the idea of deposition of BIFs from water, because even this low content of iron would likely be represented by highly-soluble iron compounds. Results of other researches also point to a low content of iron and silicon (0.002 ppm and 2.2 ppm, respectively) in seawater (Lide, 2004).

Another iron compound that is used as an indicator of an anoxic early atmosphere environment is pyrite. Pyrite cannot be formed under significant exposure to oxygen. Thick deposits of pyrite, as well as uraninite and siderite, were found in rocks older than 2.5 Ga, and with significant evidence of long surface exposure (Rasmussen and Buick, 1999). Some researches show

**Table 3.1**

Solubility of iron compounds in water (after Lide (2004))

| Chemical formula | Solubility, g/100g |
|------------------|--------------------|
| $FeCO_3$         | 0.000062           |
| $FeCl_2$         | 65.0               |
| $Fe(OH)_2$       | 0.000052           |
| $Fe(NO_3)_2$     | 87.5               |
| $FeSO_4$         | 29.5               |
| $FeCl_3$         | 91.2               |
| $Fe(NO_3)_3$     | 82.5               |
| $Fe(OH)_3$       | 0.00000000495*     |
| $Fe_2(SO_4)_3$   | 440                |

\* - calculated by the authors

**Table 3.2**

Content of iron in seawater and freshwater

| Kind of water | Content of iron, ppm |                           |
|---------------|----------------------|---------------------------|
|               | after Clark, (1982)  | after Porterfield, (1984) |
| Sea water     | 0.007                | 0.0034                    |
| Freshwater    | 0.23                 | 0.6700                    |

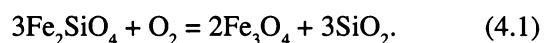


that deposits of detrital uraninite are all older than 2 Ga (Holland, 1984). In the case of pyrite deposits, different researchers also publish controversial information. Benning and Barnes (1998) select pyrite as the most abundant sulphide in the Earth's crust, which is not very consistent with known oxygen-rich atmosphere conditions during a significant period of Earth's evolution. Other authors show that pyrite was formed in the Middle Proterozoic (Shen *et al.*, 2003; Sankaran, 2004) and Late Proterozoic (Poulton *et al.*, 2004). At the same time, most of the researchers treating pyrite as an indicator of anoxic environments, are ignoring the thermodynamic characteristics of pyrite; namely, the thermal conditions of its stability.

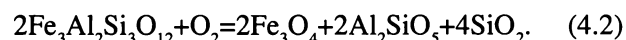
#### 4. IRON AND OXIDATION PROCESSES

Most scientists believe that the transformation of Iron(II) to Iron(III) is a result of the oxidation process with the direct involvement of oxygen. This makes a task of estimating the oxygen content at different levels within Earth extremely important. It is particularly important to estimate the oxygen levels near the Earth's surface and in Earth's atmosphere. At the same time, the surface rocks and rocks occurring at shallow depths may have direct contact with oxygen (or such oxidizing agents as water, carbon dioxide, carbon monoxide, etc.); such possibilities are extremely restricted at great depths where magma chambers are forming. Simple analysis shows that the most rock-forming minerals usually contain ferrous iron, and only among the oxides is the content of ferric iron significantly increased, and in some cases even dominant.

To characterize the oxidation state of the mantle, the oxygen fugacity parameter ( $fO_2$ ) is usually employed (Myers and Eugster, 1983; O'Neill, 1987; Hall, 1995). Oxygen fugacity helps to understand the characteristics of the mineral assemblages of forming rocks, and the conditions of their formation. Oxygen fugacity is an important parameter in terrestrial systems, because it controls the content of FeO and Fe<sub>2</sub>O<sub>3</sub>, and also the stability of metallic iron. Higher oxygen fugacity means fewer iron silicates or fewer mafic minerals, because the formation of iron oxides (mostly ferric iron oxide) would make rocks more saturated with silica. For example, the reaction of fayalite with oxygen would lead to the formation of magnetite and free silica (Hewit, 1978; O'Neill, 1987):



Reaction (4.1) is one of the reactions involved in the serpentinization process, which usually takes place at temperatures of about 473-723 K (Hess, 1955). Another reaction, that of almandine with oxygen, could also lead to the formation of magnetite and silica (Bohlen *et al.*, 1986; Harlov and Newton, 1992):



This reaction could explain the appearance of magnetite exsolution in almandine-rich metamorphic garnets below the temperature of 823 K (Brearley and Champness, 1986).

Both reactions (4.1) and (4.2) could cause the formation of magnetite and silica, two main components of BIFs. It is certain that iron deposits formed by reaction (4.2) could be Al-rich.

Oxygen fugacity is usually used for analysis of the oxidation state of iron in silicate melt and the calibration of oxygen buffers (Myers and Eugster, 1983; O'Neill, 1987, 1988; Harlov and Newton, 1992; Hall, 1995; Kadik, 1997; Wilke *et al.*, 2002). For example, Myers and Eugster (1983) defined five solid-phase oxygen buffers of the system Fe-Si-O: (1) iron-wustite (IW), (2) wustite-magnetite (WM), (3) magnetite-hematite (MH), (4) quartz-iron-fayalite (QIF), and (5) fayalite-magnetite-quartz (FMQ). In this case, the oxygen fugacity could be estimated by the incorporation of Fe<sup>3+</sup> in such minerals as garnet and spinel from the xenoliths of kimberlites and some other magmatic formations. Research shows that the value of the ratio  $Fe^{3+}/\Sigma Fe$ , which is held by numerous researchers as the indicator of the oxidation state, is less than 0.07 for the garnets from South African alkremites and eclogites (Luth *et al.*, 1990). The ratio has similar values for garnet-spinel and the low-temperature garnet lherzolites from both South Africa and the former USSR (Luth *et al.*, 1990), but is higher than 0.10 for garnets from the high-temperature garnet lherzolites of the Kaapvaal craton of South Africa (Luth *et al.*, 1990). For garnets from diamond-bearing rocks of the Kokchetav massif in Kazakhstan (Shatsky and Sobolev, 1985), the estimated value of  $Fe^{3+}/\Sigma Fe$  is -0.04. Some authors also stress the increase of Iron(III) in amphibole, depending on the oxygen content of the environment (King *et al.*, 2000), and the oxidation of the mineral, which causes the formation of magnetite and silica (Popp *et al.*, 1977).

Variations in oxygen fugacity can also affect trends of magmatic fractionation and iron enrichment or depletion in oceanic and continental basalts (Carmichael *et al.*, 1974). It was also shown that an increasing temperature always causes reduction in the Fe-O system (Lauretta and McSween, 2006). For example, in a FeO-bearing system at QFM, if oxygen fugacity is held constant and temperature is increased, FeO would be converted into iron metal, and similarly would Fe<sub>2</sub>O<sub>3</sub> be converted form Fe<sub>3</sub>O<sub>4</sub> or FeO (Lauretta and McSween, 2006). Fe<sub>2</sub>O<sub>3</sub>-bearing silicate melt will become a FeO-bearing silicate melt with heating at a constant oxygen fugacity (Kress and Carmichael, 1991). Wilke *et al.* (2002) also point at the dependence of the ferric–ferrous iron ratio in silicate melts on oxygen fugacity.

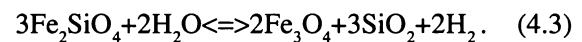
Oxidation processes are well known as the main causes of alteration of magnetic rocks and minerals (Watkins *et al.*, 1970; Mysen and Griffin, 1973; Dunlop *et al.*, 1982; Verma and Banerjee, 1982; O’Neill, 1987; Andersen and Lindsley, 1988; Bina and Prévot, 1989; Luth *et al.*, 1990; Warner and Wasilewski, 1995; Shull *et al.*, 1996; Butler, 1998; Zhou *et al.*, 2000; Benali *et al.*, 2001; Wilke *et al.* 2002; Gürsoy *et al.*, 2003; Matzka *et al.*, 2003; Shau *et al.*, 2004).

However, oxidation conditions could influence mineral composition at depths other than those of magma formation; they could cause different alterations at any stage when magma is rising to Earth’s surface, and especially during the direct contact of magma with oxidizing agents at shallow crustal depths, as well as at and near the Earth’s surface, where magma would be exposed to the atmosphere or ocean water. Another crucial condition for significant alterations to take place is associated with the process and rate of the cooling of magma. Oxidation processes could also alter solid rocks and minerals. Excellent examples of alteration of rocks in contact with the main oxidizing agents and exposed to the atmosphere are the deposition of BIFs, paleosols and red beds (Holland, 1984). These rocks, based on their iron oxides content, are considered by numerous authors to be markers of the oxygen level in the atmosphere (e.g., Kasting and Donahue, 1981; Holland, 1984).

At the same time, it is not necessary to have only oxygen as an oxidizing agent. For example, a significant part of the Precambrian, including both Hadean and Archean periods, was anoxic (Kasting and Donahue,

1980; Holland, 1984; Kasting, 1987; Wiggering and Beukes, 1990; Eriksson and Cheney, 1992; Rye and Holland, 1998; Rasmussen and Buick, 1999; Knoll, 2003, etc.), and only starting with the Early Proterozoic (at ~2.3 Ga) did the oxygen content in the atmosphere begin rising. This means that during an anoxic period of the Earth’s evolution, free oxygen was absent and there would have been other oxidizing agents. The role of such oxidizing agents in the Early Precambrian could have been performed by water, carbon dioxide, carbon monoxide and some another sources.

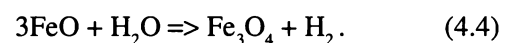
Magnetite and silica, the main components of BIFs, could also be formed by a reaction of fayalite with water within a temperature range of 923-1123 K (Hewitt, 1978):



Since reaction (4.3) is one of the main reactions in the serpentinization process, it is evident that it would also take place under temperature conditions of serpentinization, which range from ~473 to ~723 K.

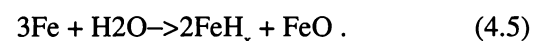
Wegner and Ernst (1983) studied forsterite hydration into serpentine at pressures of 100–300 MPa and temperatures of 461–661 K, and serpentine dehydration at temperatures of 654-773 K.

The formation of magnetite by the breakdown of FeO could take place through this reaction (Scott *et al.*, 2004):



Calculations for a 4:10 molar mixture of FeO/ water at 773 K shows (Scott *et al.*, 2004) that decomposition is nearly complete at low pressures; whereas at pressures greater than 5 GPa, there was almost no decomposition. Reaction (4.4) could be a very important one in Earth’s evolution, because the formation of free hydrogen could lead to its involvement in a subsequent formation of hydrocarbons or hydrogen that could escape from the atmosphere.

Under a pressure higher than 2.8 GPa and temperatures above 823 K, iron reacts with water to form both iron hydride and iron oxide (Yagi and Hishinuma, 1995):



Direct reaction of metallic iron with water to form iron hydride and iron oxide was also observed at pressures from 6 GPa to 84 GPa and temperatures above 1000 K (Ohtani *et al.*, 2005).

Reaction (4.5) is very important for the formation of iron hydride, which plays a significant role in the formation of the Earth's core and explains the core's density deficit (Yagi and Hishinuma, 1995; Ohtani *et al.*, 2005; Richter *et al.*, 2006).

Formation of methane is possible during a reaction involving ferrous iron oxide (or magnetite), calcite, and water (Allen *et al.*, 2001; Scott *et al.*, 2004). A possible reaction is (Scott *et al.*, 2004):



This is consistent with results of researches pointing at the possibility of the presence of significant amounts of methane in the early Earth's atmosphere (Hessler *et al.*, 2004; Ohmoto *et al.*, 2004; Catling and Claire, 2005). Formation of methane could also be produced through Fischer Tropsch catalysis, which converts CO and H<sub>2</sub> into CH<sub>4</sub> on the surface of an iron catalyst (Sekine *et al.*, 2005). The experimental results indicate that the range of temperature conditions for Fischer Tropsch catalysis is between 500 and 600 K.

The experimental results also suggest that both CO and CO<sub>2</sub> could be converted into CH<sub>4</sub> within time period significantly shorter than the lifetime of the solar nebula, at the optimal temperatures of around 550 K (Sekine *et al.*, 2005).

Other experiments show the formation of relatively high concentrations of hydrocarbon gases (methane, ethane and propane) at 673 K (50 MPa), accompanied by the oxidation of ferrous iron into magnetite (Allen *et al.*, 2001). Some authors also note that in the absence of a suitable mineral catalyst, the generation of methane is very slow (Sackett and Chung, 1979; Allen *et al.*, 2001). Experimental research shows that methane was formed from FeO, CaCO<sub>3</sub>-calcite, and water at pressures between 5 and 11 GPa and temperatures ranging from 773 K to 1773 K (Scott *et al.*, 2004). The C-H stretching band of methane was apparent by 773 K and became very strong and ubiquitous in the sample chamber by 873 K (Scott *et al.*, 2004). As a result of numerous experiments, Scott

*et al.* (2004) came to the conclusion that methane is expected to form inorganically at mantle pressures and temperatures from any carbonate species in the presence of H<sub>2</sub>O at oxygen fugacities near the wüstite-magnetite buffer. Indeed, our investigation shows that methane production is thermodynamically favourable under a broad range of high pressure-temperature conditions. Such conditions may be widespread in the mantle and can be moderated by the presence of iron-bearing phases such as Fe<sub>2</sub>SiO<sub>4</sub>-fayalite, FeS-troilite, or accessory minerals such as FeCr<sub>2</sub>O<sub>4</sub>-chromite and FeTiO<sub>3</sub>-ilmenite. It has also been shown that nickel-iron alloys can catalyze the formation of CH<sub>4</sub> from bicarbonate (Horita and Berndt, 1999). Abiotic formation of hydrocarbons at 663 K and 40 MPa with iron-bearing minerals as a catalyst was also reported by Foustoukos and Seyfried (2004). Experiments also show that in presence of iron-containing minerals and alloys at 498 - 533 K, only trace amounts of methane were produced in reactions involving aqueous CO<sub>2</sub> (McCollom and Seewald, 2003). The high-pressure genesis of hydrocarbons has been demonstrated using ferrous iron oxide (FeO), marble (CaCO<sub>3</sub>), and distilled water (Kenney *et al.*, 2002). Organic compounds were also viewed during siderite decomposition in the presence of water vapor at 573 K (McCollom, 2003). The calculations indicate that methane production is most favoured at 773 K and pressures greater than 7 GPa (Scott *et al.*, 2004). The formation of hydrocarbons occurred either by the hydrogenation of carbon or through other reactions between catalysts, carbon monoxide, carbon dioxide, and water, which probably occurred between 503-773 K (Mahfoud and Beck, 1991). Results of experiments, including the oxidation of native iron in the presence of carbon and water, demonstrate (Ikornikova, 1960) that only magnetite and ferrous iron oxide could be identified among the products, and never was pure ferric iron oxide formed. It is also shown (McCollom, 2003) that thermal decomposition of siderite during metamorphism could account for some of the reduced carbon observed in metasedimentary rocks from the early Earth.

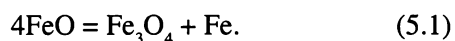
It was also demonstrated that the hydration of olivine and pyroxene minerals with the conversion of Iron(II) to Iron(III) in magnetite during serpentinization, leads to the production of H<sub>2</sub> and the conversion of dissolved CO<sub>2</sub> into reduced-C compounds including methane, ethane, propane, and heavier straight chain hydrocarbons, aromatics, and cyclic compounds (Charlou *et al.*, 2006).

Hydrogen sulfide is another oxidizing agent. Fegley (2000) shows that hydrogen sulfide ( $H_2S$ ) starts to corrode the Fe alloy grains to form troilite ( $FeS$ ) at 710 K.

The oxidation processes of iron and its compounds in most cases could be easily detected and even measured using the magnetic properties of iron, its oxides and its compounds. This relates to the fact that during oxidation, magnetic native iron ( $\alpha$ -Fe) could be converted into paramagnetic ferrous iron oxide ( $FeO$ ), which could in turn be oxidized either into an antiferromagnetic phase involving hematite ( $\alpha$ - $Fe_2O_3$ ) or one of the magnetic phases involving the formation of magnetite ( $Fe_3O_4$ ) or maghemite ( $\gamma$ - $Fe_2O_3$ ). However, even though hematite is antiferromagnetic, it has a significant natural remanent magnetization (NRM), and could form magnetic solid solutions known as ferrites.

## 5. THERMODYNAMIC CONDITIONS OF IRON OXIDES STABILITY

The role of thermodynamic conditions on iron oxides stability is known for decades in physics, chemistry, geophysics and metallurgy (Arkharov and Bulychev, 1957; Nagatha 1961; Tretyakov, 1967; Kurepin, 1975; Pilchin and Khesin, 1981; Coombs and Munir, 1990; Pilchin and Eppelbaum, 1997, Tokumitsu and Nasu, 2000; Eppelbaum and Pilchin, 2006, etc.). It is known that under specific  $P$ - $T$ -conditions, a transformation exists between ferrous ( $Fe^{2+}$ ) and ferric ( $Fe^{3+}$ ) iron (Arkharov and Bulychev, 1957; Nagatha, 1961; Tretyakov, 1967; Kurepin, 1975; Pilchin and Eppelbaum, 1997, 2004, etc.). The value of temperature accepted for this transformation at pressure 0.1 MPa is 843 K (Darken and Gurry, 1945; Arkharov and Bulychev, 1957; Nagatha, 1961; Tretyakov, 1967), and the reaction of this transformation is:



Grønvold *et al.* (1993) experimentally proved this reaction in both directions. The reaction was also accomplished in other experiments, showing that for large  $Fe_xO$  particles (wüstite) the decomposition around 530 K forms complex particles composed of layers of  $\alpha$ -Fe and magnetite, which are transformed back to wüstite at temperatures of over 833 K (Redl *et al.*, 2004). The important fact is that the reaction (5.1) does not require the presence of oxygen or any other

oxidizing agent, even though their presence may speed up the transformation of ferrous to ferric iron (TFFI). Another peculiarity is that the reaction (5.1) is not really an oxidation reaction, because along with the oxidation of two iron atoms there is a reduction of one iron atom to pure iron. The presence of giant amounts of pure iron in the Earth's inner and outer core, as well as in the cores of other terrestrial planets, proves that the oxidation process does not always take place. It is a known fact that ferrous iron is unstable under normal pressure and with temperatures below 843 K, while ferric iron is unstable above this temperature. The presence of reaction (5.1) could also be proven by the known presence of native iron in numerous investigations of some rocks and rock complexes. Native iron was found in numerous cases in volcanic, plutonic, hypabyssal, metamorphic, and sedimentary rocks; as well as in iron meteorites, eastern Siberia platform kimberlites; ultramafic and alkaline rocks, and kimberlites of the Aldan shield; ancient and young granitoids of the former USSR, granulites of Sal'nie Tundra of the Baltic Shield on Kola peninsula, volcanic pumice, basalt lavas, meteorite craters in Canada, plagiogranites of the Ore Altai Range of Russia, Cretaceous volcanics of Armenia, etc. (Pilchin and Eppelbaum, 1997). Besides this, cases of native iron were discovered in basalts from Disko Island of West Greenland (Ulff-Møller, 1990), different kinds of chondrites (Mason, 1962), in combustion-metamorphosed rocks of NW China (de Boer *et al.*, 2001), in ophiolites of eastern Canada (Deutsch *et al.*, 1977), in dolerites from Singhbhum of India (Verma and Prasad, 1975), and in lower crustal granulite xenoliths from a kimberlite pipe in W. Africa (Haggerty and Toft, 1985).

It was shown earlier that reaction (5.1) of TFFI could be used for understanding characteristics of rocks and minerals stability, thermodynamic conditions of the transformation, oxidation conditions, and magnetic properties of rocks and minerals (Pilchin and Khesin, 1981; Pilchin and Eppelbaum, 1997; Pilchin and Pilchin, 1998; Eppelbaum and Pilchin, 2006).

Other experiments gave different, but very close, values for the temperature of reaction (5.1): 843 K (Myers and Eugster, 1983), 833 K (O'Neill, 1987; Tokumitsu and Nasu, 2001) and between 800 K and 850 K (Grønvold *et al.*, 1993). Those values are similar or very close to the temperature of TFFI obtained in previous researches (Darken and Gurry, 1945; Arkharov

and Bulychev, 1957; Nagatha, 1961; Tretyakov, 1967). However, the presence of a temperature of 843 K does not necessarily guaranty the transformation between ferrous and ferric iron. The temperature of the actual transformation between iron oxides also depends on such characteristics as pressure, oxidation conditions (presence of oxygen, water, carbon oxides, etc.), and the presence of oxides of some other elements (Arkharov and Bulychev, 1957; Nagatha, 1961; Tretyakov, 1967; Kurepin, 1975; Pilchin and Khesin, 1981; Bose and Ganguly, 1995; Cohen *et al.*, 2004; Pilchin and Eppelbaum, 2004; Eppelbaum and Pilchin, 2006). This means that under low-temperature, low-pressure, and high oxidation conditions,  $\text{Fe}^{2+}$  cannot be stable; but on the other hand,  $\text{Fe}^{3+}$  cannot be stable under high-pressure, high-temperature and low oxidation conditions. It is clear that any rock or mineral containing either ferrous or ferric iron will become unstable when it is affected by temperature within the temperature range of TFFI (Pilchin and Pilchin, 1998; Pilchin and Eppelbaum, 2004). Interestingly, biotite, containing both ferric and ferrous iron is a unique mineral (Pilchin and Eppelbaum, 2004) which is one of the main iron-containing minerals of felsic rocks. The fact of the instability of iron oxides under specific  $P$ - $T$ -conditions raises questions about the conditions of present iron-containing minerals, formed in different periods of Earth's evolution. It also shows that for iron-containing rocks and minerals, it is difficult to distinguish primary and secondary rocks and minerals. Results of experimental petrology (Bowen and Tuttle, 1949; Yoder and Tilley, 1962; Green and Ringwood, 1967), as well as some geophysical researches (Pilchin and Khesin, 1981; Pilchin and Eppelbaum, 1997; Pucher and Wonik, 1998), point to the existence of reaction (5.1) in the Earth's crust and upper mantle.

Some authors helped set limits for thermodynamic conditions of TFFI. Nagatha (1961) showed that ferric iron transforms into ferrous iron even in air under temperature conditions of over 1663 K. At the same time, the temperature of TFFI significantly decreases with an increase of pressure (Arkharov and Bulychev, 1957; Tretyakov, 1967; Kurepin, 1975; Bose and Ganguly, 1995; Cohen *et al.*, 2004). Kurepin (1975) indicates that ferric iron does not crystallize from a melt at any pressure of oxygen under a lithostatic pressure of more than 2250 MPa. Even a small increase in pressure of up to 10 MPa could decrease the transformation temperature to 723 K (Arkharov and Bulychev, 1957). Some researches show that the effect

of pressure could be very significant. For example, the temperature of the eutectoid formation of wüstite from bcc-iron and magnetite decreases from 843 K at ambient pressure (Knacke, 1988) to near 430 K at  $P = 10$  GPa (Haavik *et al.*, 2000). According to another research (Shen *et al.*, 1983), wüstite forms at a temperature of 573 K from iron and magnetite when pressure is increased to 20 GPa. These results show that there are temperature and pressure limits, which do not allow ferric iron to appear, even in the presence of oxygen. Investigation performed by Tokumitsu and Nasu (2001) indicates that FeO was stable under 673 K within a vacuum. Other experiments in a vacuum (at  $10^{-8}$  MPa) under temperature conditions of 723 K also confirmed (Redl *et al.*, 2004) that the initial particles were mainly composed of wüstite ( $\text{Fe}_x\text{O}$  where  $x$  is between 0.83 to 0.96), and then completely transformed into magnetite and iron. These experiments show that the presence of oxygen or any other oxidizing agent is not required for TFFI to take place, and oxygen would usually play a more significant role only at temperatures below 673 K. This could explain the very specific role of low-temperature oxidation in rock magnetism. Hematite reduction in the presence of pyrite and CaO, leading to the formation of anhydrite and magnetite at 30 MPa and 723 K, was observed under hydrothermal conditions in a sealed gold container (Cairanne *et al.*, 2003). Results of this experiment show that hematite is unstable at a temperature of 723 K under significant pressure, even in the presence of water. Gunnlaugsson *et al.* (2002) show that the conversion from magnetite to hematite could take place under heating conditions through maghemite, and is not dependent on the presence water; which means that in this case the presence of an oxidizing agent is also not required. All these numerous facts clearly demonstrate that reaction (5.1) is related to thermodynamic conditions of iron oxides stability, rather than to oxidation processes.

Experiments involving the heating of magnetite show (Mazo-Zuluaga *et al.*, 2003) that samples treated at 793 K consisted only of well-crystallized hematite, while magnetites treated at 623 K consisted of mixtures of hematite, maghemite, and magnetite. This fact supports the assumption that for TFFI to take place, the best temperatures are those of above 673 K. The results show (Mazo-Zuluaga *et al.*, 2003) that the transformation of magnetite to hematite goes through the formation of maghemite. At the same time, there is practically no decomposition of ferrous iron oxide below approximately 523 K (Myers and Eugster, 1983).

This is consistent with other research showing that magnetization increases above 530 K, which indicates that FeO decomposes to  $\alpha$ -Fe+Fe<sub>3</sub>O<sub>4</sub> (Tokumitsu and Nasu, 2001). These temperature values coincide with the main temperature range of the serpentinization process, that of from ~473 K to ~673-773 K (Hess, 1955; Pilchin and Khesin, 1981; Pilchin and Eppelbaum, 2004). Other experimental researches show that the serpentinization process took place under a pressure of about 1 GPa and temperatures below 723 K (Bose and Ganguly, 1995; Cohen *et al.*, 2004).

Wilke *et al.* (2002) show that the iron redox ratio (Fe<sup>3+</sup>/Fe<sup>2+</sup>) decreases with temperature for a given oxygen fugacity. This gives the opportunity to use content of ferrous and/or ferric iron for identifying characteristics of oxidation conditions (Droop, 1987; Carswell and Zhang, 1999; Wilke *et al.*, 2002).

From everything of the above, it is clear that magmatic rocks in their melted conditions, and high (HP) and ultra-high (UHP) pressure metamorphic rocks should contain ferrous iron. The appearance of ferric iron in these rocks will mostly relate to the process of secondary alterations.

One of the factors influencing the stability of iron oxides is the content of such elements as Mg, Ca, and Al (Tretyakov, 1967; Pilchin and Eppelbaum, 2004; Richmond and Brodholt, 1998). Presence of MgO and CaO in solid compounds increases the stability of FeO at temperatures within the temperature range of TFFI (Tretyakov, 1967; Agee *et al.*, 1982). This is consistent with the fact that almandine (Fe-garnet) is usually found in solid solutions with pyrope (Mg-garnet) and/or grossular (Ca-garnet). Solid solutions of Al and Fe<sup>3+</sup> oxides are also known (Andreozzi *et al.*, 2001), that could be proven by the content of ferric iron in such minerals as kyanite and sillimanite (Bohlen *et al.*, 1991), and Al-hematite and Fe-corundum (Majzlan *et al.*, 2002).

Some of the most recent researches also point to higher Fe<sup>2+</sup>/Fe<sup>3+</sup> values in spinel from mantle peridotite than those of spinel from volcanic rocks (Kamenetsky *et al.*, 2001, *etc.*).

The above facts illustrate that ferrous iron would not be stable in rocks and minerals formed in the upper and middle Earth crust at temperatures between 473-523 K and 843 K, which could be accepted as the main

temperature range for TFFI. Similarly, ferric iron would not be stable in rocks and minerals forming in the Earth's lower crust and upper mantle. It is also evident that rocks and minerals formed at great depth could become subjects of secondary alterations, including TFFI, during their eruption or exhumation to Earth's surface or layers within the upper crust. This is in good compliance with the known fact that magnetite and ferric iron oxide (Fe<sub>2</sub>O<sub>3</sub>) are secondary minerals (Nagatha, 1961; Pechersky *et al.*, 1975), as well as some other ferric iron-containing minerals (Pilchin and Eppelbaum, 2004).

Droop (1987) shows that in most cases, a microprobe cannot distinguish between atoms of different valence states, but in many cases it is possible to calculate the proportion of ferric iron required for satisfying the charge balance. Some authors indicate the importance of estimations of the relative content of ferric iron (Fe<sup>3+</sup>/Fe<sup>2+</sup>) for geothermobarometry (Carswell and Zhang, 1999; Banno *et al.*, 2000). Carswell and Zhang (1999) state that ignoring the ferric iron content in omphacite could lead to errors of temperature estimation by more than 100 K. In some cases such an error could be even higher, offset by more than 200 K (Luth *et al.*, 1990).

There is other data that strongly suggests that an increase of iron content may significantly reduce the stability temperature and pressure for different rocks and minerals. Such an increase of iron content may reduce the stability temperature of orthopyroxene by more than 623 K (Ross and Huebner, 1979). Presence of iron oxides and Mg-oxide significantly reduce the stability pressure of albite (Newton and Smith, 1967). Increase of acmite content in jadeite reduces the pressure of albite stability by 30 MPa for 10% of acmite and 160 MPa for 40% of acmite content at approximately 873 K (Newton and Smith, 1967). The experiments of Liu and Bohlen (1995) illustrate that the addition of as much as 40% of acmite component to jadeite extends pyroxene stability by almost 300 MPa at 1173 K.

Since most scientists believe that *P-T*-conditions of the breakdown of albite are strongly related to conditions of the formation of eclogite (Green and Ringwood, 1967; Wain *et al.*, 2001; Bruno *et al.*, 2002), it is clear that the increase of iron content, and especially its ferric content, may significantly reduce the pressure of eclogite formation.

The increase of Cr content in some indicator minerals is also related to ferrous – ferric iron transformation. It is a known fact that the presence of free FeO could play a crucial role in the formation of the immobile form Chromium(III) from its mobile form of Chromium(VI) (Fendorf and Zamoski, 1992). Chromium(III) and Chromium(VI) are the only stable forms of chromium in natural environments (Fendorf and Zamoski, 1992; Yang and Enami, 2003). The stable forms of chromium are characterized by the high solubility of Chromium(VI) and the low solubility of Chromium(III), especially in the presence of Iron(III) at neutral pH levels (Eary and Rai, 1988). This could explain why Cr is mostly found in places with high almandine content. Chromium(III) easily precipitates as  $\text{Cr}(\text{OH})_3$  or as the solid solution  $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$  in alkaline or even slightly acidic conditions (Rai *et al.*, 1987). These data demonstrate that for the formation of Chromium(III), the presence of Iron(II) is necessary to activate a reaction of the Chromium (VI) => Chromium (III) transition. However, the Iron(II) should be free and not as a part of a compound. Therefore, it is necessary to have conditions for the breakdown of Iron(III)- or Iron(II)-containing minerals, or the transformation of Iron(III) to Iron(II). Moreover, Iron(II) is a commonly used reductant for Chromium(VI) in wastewater treatment. In natural environments, Iron(II) can be released from primary silicates and oxides, such as muscovite and biotite; and secondary layer silicates, such as vermiculite, illite, smectites, and chlorite (Eary and Rai, 1989). The breakdown of almandine could also lead to the release of FeO, which could explain the presence of Chromium(III) in such indicator minerals as Cr-diopside and garnet.

All these facts are also consistent with the conclusion that active metals replace less active metals in compounds. Pilchin (1998) noted that the release of alkali metals during some processes (for example serpentinization) leads to the replacement of alkaline earth metals by alkali metals in substitution reactions. This fact was proven by strong negative correlation between contents of alkali earth metals and alkali metals with a correlation coefficient of  $r = -0.9$  for the main types of magmatic rocks (Pilchin, 1998).

## 6. IRON AND THE EVOLUTION OF EARLY EARTH

Now we know that early Earth evolution was characterized by an essentially anoxic atmosphere. We

also know that the relationships between iron oxides depend on thermodynamic conditions; most importantly that of temperature. Let us analyse available data to find out the role of iron in the formation and evolution of the early Earth.

An important fact to consider in the analysis of conditions for TFFI during the early Earth evolution is the stripping away of the atmospheres of terrestrial planets by the solar wind during the very beginning of planetary evolution (Bennett *et al.*, 2004). This means that there was no atmosphere for some time during the formation and evolution of early Earth. Another fact, which should be taken into account, is the temperature growth during accretion and differentiation of terrestrial planets (Aleinikov *et al.*, 2001), as well as during the decay of long-living radioactive isotopes.

### 6.1. What was going on in the solar nebula?

The problem of iron oxides stability during the formation and evolution of early Earth could give us important information on processes of rocks and minerals formation, as well as on the differentiation of Earth's layers. It is obvious that such a research requires information on the iron oxides content in material used for the Earth's formation (see Chapter 2), as well as temperature conditions during the formation and evolution of early Earth. Such research could yield some additional information about the existence and role of TFFI through reaction (5.1) during the early Earth evolution. McCall (1973) noted that most meteorites contain FeO, and only a few contain  $\text{Fe}_2\text{O}_3$ ; iron and stony-iron meteorites comprise 5% and 1% of all meteorites, respectively (see Table 2.3). Also, the initial temperature in the solar nebula at distances from Sun, where now the terrestrial planets are, was relatively high (Table 6.1). In Table 6.2 three other models of temperature and pressure distribution in the inner part of the solar nebula are presented.

Different models demonstrate that the temperature in the nebula during the accretion period could have reached values of 900-1400 K (Deming, 2002) and 1400 K (Humayun and Cassen, 2000) at the distance of where Earth is from the Sun (1 AU). Boss (1998) showed that, for his model, temperatures within the inner part of the protoplanetary disk were in the range of 500–1500 K. Kerridge (1977) indicated that the distribution of iron among planets and meteorites can probably be adequately modeled by condensation and

fractionation under equilibrium conditions of above ~700 K. Analysis of these temperature data in the solar nebula shows that only for one model (Table 6.2) is the temperature at a distance of 1 AU near the lower bound (~470 K) of the required temperature conditions for reaction (5.1), while for all other models (see Tables 6.1 and 6.2) it is within the temperature interval of reaction (5.1). However, taking into account that magnetite could be formed in the solar nebula from native iron at a temperature of about 370 K (Fegley, 2000), it is clear that for all the models referenced above iron oxides were within the temperature interval of TFFI right before the start of Earth formation.

A comparison of temperature in the solar nebula (see Table 6.1) with the main temperature range of TFFI (between 473-523 K and 843 K) indicates that the

temperature at the beginning of the formation of Mars was at the lowest limit of the temperature range of TFFI and under conditions of ferric iron oxide stability. The temperature at the beginning of Earth's formation was within the temperature range of TFFI and also under conditions of ferric iron oxide stability. The temperature at the beginning of Venus' formation was near the upper limit of the temperature range of TFFI and under conditions of ferric iron oxide stability as well. The temperature at the beginning of Mercury's formation was above both that of the upper limit of the temperature range of TFFI and of ferric iron oxide stability. This means that the material of the solar nebula at a distance of 1 AU from the Sun was in the temperature range of TFFI, and its material could contain a significant amount of ferric iron oxide either as magnetite or as hematite.

**Table 6.1**

Surface (or cloud tops) temperature of terrestrial planets and temperature in solar nebula at the distance of the planets

| Object  | Temperature in solar nebula at the distance of the planets, K |                                 |                   | Present average surface (or cloud tops) temperature, K |
|---------|---|---------------------------------|-------------------|--|
|         | After Kaufmann, 1994  | After Kaufmann & Freedman, 1999 | After Kaler, 1994 |  |
| Mercury | ~1400   | ~1200                           | 1400              | 700 (day side),<br>100 (night side)                    |
| Venus   | ~750  | ~750 K                          | 800-850           | 740  |
| Earth   | ~650-700  | ~650-700                        | 600               | 290  |
| Mars    | ~450-460  | ~500                            | 500               | 240  |
| Jupiter | ~170  | ~170                            | 150               | 125  |
| Saturn  | ~90-95  | ~90-95                          | 85                | 95   |
| Uranus  | ~50   | ~50                             | 50                | 60   |
| Neptune | ~40   | ~40                             | 45                | 60   |
| Pluto   | ~30   | ~30                             | 30                | 40   |

**Table 6.2**

Temperature and pressure distribution in inner part of solar nebula: three models

| Distance from Sun, AU | Temperature, K | Pressure, MPa     | Reference                  |
|-----------------------|----------------|-------------------|----------------------------|
| 0.01                  | 7600           | $7 \cdot 10^{-2}$ | Lewis, 1974                |
| 1                     | 600            | $10^{-5}$         |                            |
| 0.01                  | 2200           | $3 \cdot 10^{-3}$ | Cameron, 1995              |
| 1                     | 470            | $4 \cdot 10^{-6}$ |                            |
| 0.01                  | 1500           | $4 \cdot 10^{-4}$ | Willacy <i>et al.</i> 1998 |
| 1                     | 600            | $10^{-6}$         |                            |



At the same time, all terrestrial planets contain giant quantities of iron, mostly within their iron cores (see Tables 2.5 and 2.6). The presence of giant quantities of metallic iron points at the reduction conditions during the formation of those cores. It was shown above, based on the density distribution of iron, iron oxides and iron-containing minerals (see Table 2.7), that metallic iron would likely have a higher concentration in the solar nebula closer to Sun (at the location of Mercury), and iron oxides, iron sulfides, and iron silicates would likely have higher concentrations at the location of Mars; and concentrations of both would then be found somewhere between at the locations of Earth and Venus. This is consistent with the fact that conditions favouring TFFI reduce at the location of Mercury, with the presence of temperatures above those necessary for reaction (5.1) and the presence of an almost entirely metallic iron core within Mercury, with nearly complete absence of iron-containing minerals in its mantle. At the same time, at the location of Mars, where the temperature in the nebula was near the lower limit but within the temperature range for reaction (5.1), the content of metallic iron is minimal, while the content of iron-containing minerals in the mantle is maximal among terrestrial planets. This also coincides with the fact that the soil of Mars is composed 18% of  $Fe_2O_3$  (Anderson, 1990).

For comparison of iron content in the mantle and crust of terrestrial planets, corresponding values of these concentrations were calculated (Table 6.3). Values of iron concentration in terrestrial planets compiled in Tables 2.5 and 2.6 were used for the calculations.

The data presented in Table 6.3 illustrate the abovementioned trends of the distribution of iron content in the core and crust with mantle of terrestrial planets, with an anomalous content for Earth. Since

the Earth's metallic core takes up a much larger percentage of the Earth's mass than the percentage of iron and stony-iron meteorites from all meteorites (see Tables 2.4 and 2.5), there should have been some further processes of metallic iron extraction during the evolution of Earth. Such distribution of iron in terrestrial planets is also consistent with the possibility that higher temperatures in the inner part of the solar nebula may have led to the condensation of most Fe into its metallic form, with very little oxidation into Iron(II) or Iron(III) (Cox, 1990). Reaction (5.1) could obviously play a significant role in the reduction of iron. This coincides with the fact that all minerals mentioned in Table 2.7, except for almandine, are well known to be found both in Earth and in meteorites. At the same time, almandine (iron garnet) is a very typical mineral in kimberlites (Schulze *et al.*, 2000). Almandine-rich garnets are also widely distributed in regions of orogenic belts. Such almandine-rich garnets were found in the Aegean region (Perraki and Mposkos, 2001), New Zealand (White, 1996), La Ronge domain of Trans-Hudson Orogen (Yang *et al.*, 1998), North Jay Pluton of Maine (Dutrow *et al.*, 1999), Gualala basin of California (Schott and Johnson, 2001), Branisko Mts. of Western Carpathians (Faryad, 1999), Bårdsholmen, WGR, Norway (Engvik *et al.*, 2000), Dabie Shan, China (Schmid, 2000), Qaidam eclogite belt, NW China (Song *et al.*, 2003), Bahia, Brazil (Osako *et al.*, 2001), Maksyutov Complex, S. Ural Mountains (Leech and Ernst, 2000), Mozambique belt, Tanzania (Johnson *et al.*, 2003), Sanbagawa metamorphic belt. Almandine-rich garnets were also found in micro-diamond-bearing regions (Dobrzhinetskaya *et al.*, 1995). These data show that almandine is widely distributed in Earth.

## 6.2. It was hot

Estimation of the value of the combined energy of planetary accretion, gravitational settling of Earth's

**Table 6.3**

Estimated values of iron content in the mantle and core of terrestrial planets

| Planet  | Mass of planet, kg   | Mass of iron in crust and mantle, kg      | Mass of iron in core, kg |
|---------|----------------------|---|--------------------------|
| Mercury | $3.30 \cdot 10^{23}$ | 0   | $2.09 \cdot 10^{23}$     |
| Venus   | $4.87 \cdot 10^{24}$ | $5.52 \cdot 10^{22}$                      | $1.31 \cdot 10^{24}$     |
| Earth   | $5.97 \cdot 10^{24}$ | $2.1 \cdot 10^{23}$ - $2.8 \cdot 10^{23}$ | $1.73 \cdot 10^{24}$     |
| Mars    | $6.42 \cdot 10^{23}$ | $1.07 \cdot 10^{23}$                      | $5.50 \cdot 10^{22}$     |

metallic core, meteorite impacts, and possible collision with a Mars-size body, shows that the value of energy was sufficient to melt the entire Earth during its accretion (Lubimova, 1968; Halliday, 2000; Valley *et al.*, 2002; Walter and Trønnes, 2004). An analysis of geothermal researches indicates (MacDonald, 1962; Lubimova, 1968) that there are two main points of view regarding the earliest Earth temperature condition: 1) hot origin of Earth (the planet was completely melted initially); 2) cold/warm origin of Earth (the planet was hot but not completely melted). Analysis of type B coarse-grained calcium-aluminum-rich inclusions (CAIs), the oldest known materials to have formed in the solar system, shows that once type B CAIs precursors have been condensed from a solar nebula, they were reheated at 1523–1723 K (Richter *et al.*, 2006). Another fact supporting the significant increase of temperature during planetary accretion shows (Scott and Krot, 2005c) that meteorites of types 4-6 were heated to 900-1300 K.

This coincides with the data of other authors indicating that at the time of core formation, Earth (and possibly Venus and Mars) may have been entirely molten (Jakosky, 1999; Walter and Trønnes, 2004). Birch (1965) has also shown that for the formation of the Earth's iron core, it is necessary for the temperature of the Earth's layers to be above that of the melting point of iron at some point of Earth's evolution. Other researches demonstrate that Earth, at some point of its early evolution, was covered by a magma-ocean (Safronov, 1978; Abe, 1997; Pollack, 1997; Solomatov, 2000; Walter and Trønnes, 2004, etc.), which was a few hundred kilometres deep (Safronov, 1978; Walter and Trønnes, 2004, etc.). A magma-ocean was also developed on other terrestrial planets (Condie, 1989a, McSween, 1993; Lauretta and McSween, 2006), the Moon (McSween, 1993; McSween, 1999; Bennett *et al.*, 2004), and Vesta (Richter and Drake, 1997). Some scientists believe that such a magma-ocean could exist for about 1 to 10 My (Spohn and Schubert, 1991). Other investigators believe that the magma-ocean could remain for 100-200 My (Abe, 1997; Pollack, 1997) and even longer (Solomatov, 2000).

The main controversy in the Earth's thermal regime after the Hadean period is mostly related to problems of the rate of cooling of early Earth. Some scientists believe that the cooling of the Earth was completed very quickly (Davis, 1990; Spohn and Schubert, 1991; Franck, 1992; Sleep *et al.*, 2001), but

according to another point of view, significant cooling took place during a long time interval (Abe, 1997; Pollack, 1997; Solomatov, 2000).

It is obvious that under conditions of magma-ocean, ferric iron had negligible chances for survival. This means that the only way for ferric iron to appear would be its formation through TFFI, when the cooling of Earth's surface dropped the temperature to a value below 843-723 K; this also means that any mineral containing Iron(III) could only be of secondary origin. Since the atmosphere during the early period of Earth evolution was essentially anoxic; there was no other way for ferric iron to appear.

It is also evident that the time of solidification of the magma-ocean and cooling of Earth's upper crustal layers is crucial for the development of many important processes including the origin of the ocean and the formation of rock magnetism. Many scientists consider that even though at some point the Earth's surface was covered by a magma-ocean, it cooled really fast by geologic time measures (Spohn and Schubert, 1991). Unfortunately, some researchers did not take into account such facts as the necessary time for Earth's differentiation, cooling rates, and the release of energy by long- and short-living radioactive elements. For example, analysis of geothermal data indicates that the Earth energy released by long-living radioactive elements would create conditions of heating of Earth's interiors (Lubimova, 1968). This is consistent with the formation of komatiite magmas at the end of the Archean, which suggests a temperature maximum in the mantle. Calculations presented by Birch (1965) and Lubimova (1968) demonstrate that the temperature within Earth could have increased to that of the melting point of iron during the first 0.5-1.0 billion years after the formation of Earth was completed. All these facts do not support theories of a fast cooling of Earth's layers.

The cooling rate of the mantle, estimated by different researchers, varies from 0.03 K/Ma (Peck *et al.*, 2001) to 0.20 K/Ma (Condie, 1989b). Estimations for the cooling rates of magmatic and metamorphic formations and regions of Earth, performed by various authors, illustrate that they vary from 0.2 K/Ma to hundreds of K/Ma, but in most cases the estimated values are in single units of K/Ma. Interestingly, an estimation of the cooling rates for Mars and Venus gave values of 0.25 K/Ma and 0.10 K/Ma, respectively (van

Thienen *et al.*, 2005). At the same time, estimations of the cooling rate in the Adirondack Highlands vary from very fast – over 200 K/Ma (Storm and Spear, 2005), to slow – 4 K/Ma (Johnson *et al.*, 2002) and very slow – 0.5-1.0 K/Ma (Mezger *et al.*, 1989). Some authors note that the cooling rates are faster for high temperatures and much slower for lower temperatures (Zeck, 1996; Monié *et al.*, 1997; Christoffel *et al.*, 1999; Okudaira *et al.*, 2001; Meert *et al.*, 2003; Schmitt *et al.*, 2004; Zhao *et al.*, 2004). A comparison of the cooling of a size of any magmatic effusive or intrusive complex, metamorphic complex, or orogenic belt with the cooling of a magma-ocean covering the entire Earth with a depth of a few hundred kilometers, shows that the cooling rate of the magma-ocean should be thousands, millions, or even billions of times slower. It should also be taken into account that the magma-ocean could lose heat energy only through radiation and contact with the atmosphere.

### **6.3 What happened with the atmosphere and free oxygen back then?**

From all of the abovementioned, it follows that the most important factors for TFFI are temperature, pressure, and the presence of such oxidizing agents as oxygen, water, and carbon dioxide. This makes thermodynamic conditions (temperature and pressure), and composition of the ocean and atmosphere extremely important for any research on iron, and iron-containing rocks and minerals at or near Earth's surface, and in any crust layer in which contact between solid rocks and either the ocean or atmosphere (or both) could take place. These problems of the thermodynamic conditions and composition of the ocean and the atmosphere are of extreme importance to numerous processes, most of which are outside the scope of this investigation.

This is the reason why problems related to the formation and composition of both the early atmosphere and ocean, are discussed in this chapter briefly, and from the point of view of their importance to the presence, formation, composition, preservation, and changes of iron compounds.

The stripping down of the Earth's atmosphere by the solar wind during the very beginning of Earth evolution (Bennett *et al.*, 2004) means that all elements and compounds, which were later involved in the formation of a new atmosphere, were bonded in solid

compounds with other elements, and were later released through different features and processes. Significant amounts of compounds containing the oxidizing agents mentioned could also be delivered to Earth by comets, hydrous asteroids, phyllosilicates migrating from the asteroid belt, and hydrous minerals and carbonates from carbonaceous chondrites (Drake, 2005).

Any estimations of the possible atmosphere composition could only be made from the period starting from the existence of the magma-ocean. It is obvious that at the time of the magma-ocean, there was no chance for the presence of a water-ocean, and all or almost all of the water existed in the atmosphere as vapour. This is consistent with other researches (Humayun and Cassen, 2000) showing that at some point of the evolution of terrestrial planets, almost all fluids were present as vapour. This indicates that at some point of the Earth evolution even the state of water, whether gaseous or liquid, is important. It is also likely that all kinds of magmatic activity during the formation and existence of the magma-ocean would cause degassing of part of the content of carbon (as CO<sub>2</sub>, CO, and CH<sub>4</sub>), sulphur (as SO<sub>2</sub> or sulphur vapor). This would make the atmosphere during the time of the magma-ocean very dense. A simple estimation of the atmospheric pressure at the time of the magma-ocean gave a minimum value of about 35 MPa. This value was calculated by taking into account that all current ocean and ground water existed as vapour- and all carbon dioxide now tied up in carbonates existed as gas- in the atmosphere; which means that this value should be considered as the minimum value of atmospheric pressure, since the water content of Earth is much greater (Drake, 2005; Ohtani, 2005). For example, an estimate based on the water storage potential of minerals in the silicate Earth is about that of 5 – 6 Earth oceans (Ohtani, 2005), but the temperature of the magma-ocean was too high for some hydro-silicates to hold their water. The computations of Stimpfl *et al.* (2004) and Drake (2005) demonstrate that the amount of water adsorbed in the Earth during accretion could be as much as that of 1 – 3 Earth oceans. This means that atmospheric pressure at the time of the magma-ocean could have been a few times higher than the value estimated above. This coincides with estimations made by other authors that show that only the carbon dioxide tied up in carbonate rocks could cause a pressure as high as ~6 MPa (Ronov and Yaroshevsky, 1967; Holland, 1978; Kasting and Ackerman, 1986), and 8 MPa (Kaler, 1994).

Estimations of the partial pressure of carbon dioxide by other authors show that this value could be as high as 21.5 MPa (Zhang and Zindler, 1993) or even of 10-100 MPa (Sukumaran, 2001). Pollack (1997) has shown that at some point in the Hadean, all water was vaporised. Abe (1993) estimated that the concentration of H<sub>2</sub> and H<sub>2</sub>O in the Earth's atmosphere right after accretion would be capable of generating pressure of about 20-30 MPa. Other authors estimated the water pressure at 10 to more than 30 MPa (Zahnle *et al.*, 1988), and ~56 MPa (Liu, 2004). All these estimations show that the density and pressure of the atmosphere at the time of the magma-ocean could have been very high. Interestingly, both carbon dioxide and water vapour are among the most important greenhouse gases, but, even though at some point of Earth's atmospheric evolution the concentration of these gases in the atmosphere was very high, it did not lead to a run-away greenhouse effect. It is clear that the evolution of the atmosphere, as well as the formation of the water-ocean to follow, strongly depends on the rate of the solidification and cooling of the magma-ocean. This means that the presence of an extremely dense atmosphere at some point of Earth's evolution should be considered fact. Of course, it is very important to investigate both how such a dense atmosphere was formed and how it changed after the solidification and cooling of the magma-ocean to its present content and

conditions. The abovementioned is in agreement with the data of Deming (2002) showing that widespread hydration of the oceanic crust did not occur until about 3.0 Ga, and volumes of water sufficient to cover the Archean analogues of mid-ocean spreading ridges did not exist prior to this time. It is also obvious that the formation of the ocean could take place only under thermodynamic conditions allowing for the presence of liquid water on the Earth's surface. Thermodynamic conditions of water are presented in Figure 6.1. For the value of the density of water at the beginning of its boiling, the value 958.36 kg/m<sup>3</sup> at boiling point 373 K and pressure 0.1 MPa (Speight, 2005), was accepted. Extrapolation for the boiling point curve was used, because the maximum pressure for which the boiling point was defined is 6.895 MPa. The data in Figure 6.1 display that the formation of the ocean took place when the temperature of the atmosphere and the Earth's surface was between 395 and 615 K.

Results of modeling (Stimpfl *et al.*, 2004) show that only 0.25% of an ocean of water could be adsorbed at 1000 K, 1% of one Earth ocean could be adsorbed at 700 K, and only 3% at 500 K. This means that until Earth's surface cooled, there were no conditions for significant absorption of water by cooling crustal rocks. The formation of the ocean took place sometime between the solidification of the magma-ocean and the

| Object  | Temperature in solar nebula at the distance of the planets, K |                                 |                   | Present average surface (or cloud tops) temperature, K |
|---------|---|---------------------------------|-------------------|--|
|         | After Kaufmann, 1994  | After Kaufmann & Freedman, 1999 | After Kaler, 1994 |  |
| Mercury | ~1400   | ~1200                           | 1400              | 700 (day side),<br>100 (night side)                    |
| Venus   | ~750  | ~750 K                          | 800-850           | 740  |
| Earth   | ~650-700  | ~650-700                        | 600               | 290  |
| Mars    | ~450-460  | ~500                            | 500               | 240  |
| Jupiter | ~170  | ~170                            | 150               | 125  |
| Saturn  | ~90-95  | ~90-95                          | 85                | 95   |
| Uranus  | ~50   | ~50                             | 50                | 60   |
| Neptune | ~40   | ~40                             | 45                | 60   |
| Pluto   | ~30   | ~30                             | 30                | 40   |

Fig. 6.1. Thermodynamic conditions of water. (1) The conditions of equilibrium of water for its density 958.36 kg/m<sup>3</sup> at start of boiling at 373 K and pressure 0.1 Mpa, (2) The conditions of equilibrium of water with density 1000 kg/m<sup>3</sup>, (3) Boiling temperature of water (extrapolation using data of Speight (2005)).

Early Proterozoic glaciation, when the temperature of Earth's surface dropped to below the freezing temperature of water.

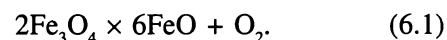
A giant quantity of oxygen on Earth is obviously present, since it is one of the two most common elements in Earth's rocks and minerals, and composes about 29-30 % of the Earth's mass. This means that the anoxic environment of Earth's early atmosphere is related not to the lack of oxygen content, but to the lack of free oxygen content, because oxygen is always involved in different reactions with rocks, minerals, and elements of the Earth strata. This could also mean that the main oxidation processes at the Earth's surface and uppermost layer/layers of young crust involving oxygen were completed first, before the quantity of free oxygen in the atmosphere began to grow.

Iron and oxygen together compose about 62-63% of the Earth's mass, and, since the first Primordial atmosphere was blown away by solar wind, FeO and Fe<sub>2</sub>O<sub>3</sub> could have been important compounds of oxygen in the solar nebula. Let us estimate the possible amount of oxygen preserved for the Earth within iron-containing compounds. Table 6.4 displays the content of oxygen in iron oxides, magnetite, and some Fe-O-rich silicates. It is obvious that the content of oxygen in iron oxides and magnetite is significant, but its quantity is significantly lower in ferrous iron oxide than it is in ferric iron oxide, or Fe-O-rich silicates.

As it was discussed above, it is most likely that at the distance of 1 AU from the Sun, there was a negligible amount of metallic iron, and most iron was present in iron oxides and some other iron compounds. On the other hand, temperatures in the solar nebula at a distance of 1 AU right before the beginning of accretion were in the range of ferric iron oxide stability.

This means that the majority of iron oxides in this part of the solar nebula could have been represented by ferric iron oxide or magnetite. This is consistent with data of Table 2.7, which demonstrates that the density of ferric iron oxide and magnetite is significantly lower than the density of metallic iron and ferrous iron oxide, which would be more strongly attracted by the Sun. This allows for the possibility to estimate the minimal amount of oxygen preserved by iron compounds in the Earth, assuming that all oxygen was bonded with iron in ferrous iron oxide, and the maximal value of oxygen preserved by iron assuming that all oxygen was bonded with iron in pure ferrosilite. Our estimations illustrate that the minimum amount of oxygen bonded with iron (as FeO) in Earth's crust and mantle is 6.0-8.0·10<sup>22</sup> kg (1.01-1.34 % of Earth's mass) and the estimated amount of oxygen bonded with iron as Fe<sub>2</sub>O<sub>3</sub> in Earth's crust and mantle is 9.0·10<sup>22</sup>-1.2·10<sup>23</sup> kg (1.52-2.01 % of Earth's mass). The estimations of the amount of oxygen released by iron oxides during the formation of Earth's iron core are a minimum of: 4.943·10<sup>23</sup> kg (8.3% of Earth's mass), for a FeO to Fe transformation; and a value of 7.415·10<sup>23</sup> kg (12.45% of Earth's mass), for a Fe<sub>2</sub>O<sub>3</sub> to Fe transformation. Our estimations of the total content of oxygen bonded with iron assuming that during accretion iron was only present as FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>SiO<sub>4</sub>, or Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> gave values in the range of 8.86-9.62%, 13.29-14.43%, 17.71-19.25%, or 26.57-28.87% of total Earth's mass, respectively. Interestingly, the total Earth's content of oxygen was estimated at about 29-30 % of the total Earth mass (see Chapter 2).

Free oxygen could also be released during the heating of magnetite above the temperature of ferric iron stability, through reaction:



**Table 6.4**

Content of oxygen in iron oxides and some iron compounds

| Iron oxide                   | Chemical formula                               | Content of oxygen, % |
|------------------------------|--|----------------------|
| Ferrous iron oxide           | FeO  | 22.222               |
| Magnetite                    | Fe <sub>3</sub> O <sub>4</sub>                 | 27.586               |
| Hematite (ferric iron oxide) | Fe <sub>2</sub> O <sub>3</sub>                 | 30.000               |
| Fayalite                     | Fe <sub>2</sub> SiO <sub>4</sub>               | 31.373               |
| Ferrosilite (pure)           | Fe <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> | 36.364               |

Since the initial temperature in the nebula at the location of the formation of Earth was in the range of stability of ferric iron oxide, it is possible that a significant amount of iron in the nebula was present in this form, making the oxygen content at the location of Earth higher than at that of Mercury or Venus. At the locations of Mercury and Venus, which actually had initial temperatures in the nebula prior to their formation at about the upper bound of ferrous iron stability for Venus, and within the range of ferrous iron stability for Mercury. However, the content of bonded oxygen would be much less than at the location of Earth. At the same time, the absence of a significant iron core on Mars means that most oxygen initially bonded to iron was not released, and therefore Mars did not collect much free oxygen in its atmosphere.

#### **6.4. Iron and evolution of early Earth**

It was shown earlier (see Eqs. (4.1) and (4.2)) that magnetite and silica could be formed during the oxidation of fayalite and almandine. However, these reactions require the presence of free oxygen, which was absent from the early Earth atmosphere. This means that reactions (4.1) and (4.2) could not have played any significant role in the formation of BIFs of the Archean and earliest Paleoproterozoic (before about 2.3 Ga). Instead, reactions involving water (4.3), carbonates and water (4.6), as well as those of carbon oxides and water, could have played a crucial role in the formation of BIFs during this period of time. It is obvious from Chapter 4 that the mentioned reactions are within the temperature range of TFFI. This fact, along with the thermodynamic conditions of TFFI, indicates that the formation of BIFs in the Early and Middle Precambrian also took place under temperature conditions within the temperature range of TFFI. This means that it is possible that in regions of deposition of BIFs, the surface temperature was within the range of TFFI (mostly between 473-523 K and 673-843 K). It also means that the fact that BIFs were deposited could be used as a marker of specific temperature conditions of the surface and atmosphere. This is consistent with the analysis of temperature conditions of the formation of the water-ocean and the composition of the atmosphere (see paragraph 6.3).

It should be taken into account that from the start of Earth's accretion to the time that Earth's surface cooled to below 843-723 K, there was no chance for the presence of any significant amounts of ferric iron oxide. It is possible that the time of the first formation

of magnetite in BIFs marks the time in Earth evolution when the surface temperature dropped below 843-723 K for the first time. The only mineral, which can possibly gain its ferric iron before the formation of magnetites, is biotite, one of the main rock-forming minerals of the Early and Middle Precambrian. This means that the appearance of the first Algoma-type BIF marks the point in time when the surface temperature cooled to below the upper bound of the temperature range of TFFI. It is also likely that during the formation of each BIF, the surface temperature in the area of its formation was within the temperature range of TFFI. This coincides with the known fact that both Algoma- and Superior-type BIFs are characterised by positive europium anomalies, which are the indicators of high-temperature alteration of volcanic rocks (Graf, 1978; Derry and Jacobsen, 1990; Klein and Beukes, 1992; Huston and Logan, 2004). Huston and Logan (2004) indicate that Algoma-type BIFs are characterized by much larger europium anomalies (greater than 1.8) than Superior-type BIFs, which could point to a higher surface temperature during the periods of the formation of the earliest BIFs. Earth's surface temperature was not necessarily within the temperature range of TFFI during the entire time span of the deposition of BIFs from 3.85 Ga until 1.85-1.80 Ga. However, at the time of deposition, BIFs would indeed have to have been within the temperature range of TFFI. This means that the first BIF deposition was also the first process of the formation of magnetic minerals, and the beginning of rock magnetism formation. Such processes as the relatively wide-spread distribution of komatiite magmatism in the Late Archean, picrite magmatism in the Early Proterozoic, and Late Archean global magmatic event taking place on all Archean cratons around 2.5-2.7 Ga are also pointing to the possibility of high surface temperatures (regional or local).

Since early atmosphere was essentially anoxic, the formation of the giant quantities of BIFs by oxidation involving oxygen was not possible, and their formation was most likely related to TFFI. It is evident that the formation of any remanence magnetization during the Archean could not be stable and was not preserved until present time, because of the presence of relatively high temperatures, low cooling rates, and a possible periodic re-heating of rocks. This coincides with paleomagnetic and rock magnetic measurements of late Archean rocks from the Hamersley basin, Western Australia, showing the presence of a stable component at about 663 K, which was interpreted as the post-tilting thermal

overprint (Sumita *et al.*, 2001). One of the best examples of secondary changes in magnetization or different cooling rates in magmatic rocks of the Middle Precambrian is the presence of normal (N) and reversed (R) magnetization in the dykes of the Matachewan dyke swarm of Canada (~2.45 Ga). For both N and R dykes, the baked country rocks carry the same remanence as the dykes, and dykes of opposite polarity exist in close proximity (Bates and Halls, 1991). In a few cases, N dykes are found to crosscut R dykes (Bates and Halls, 1991). The Matachewan dyke swarm was formed during a period of about 5 Ma (Bates and Halls, 1991). If we accept that N dykes represent the second period of the generation of dykes, there should have been re-heating conditions during the emplacement of N dykes, especially in cases where N and R dykes are located in close proximity and in cases where N dykes crosscut R dykes. This means that R dykes should show some secondary changes. However, the absence of such changes suggests that the formation of both kinds of dykes took place during a single event, but with different rates of cooling or different temperatures for TFFI in those dykes. Surely, such variations and different local cooling rates could have caused TFFI to take place at different temperatures from ~843 to ~473 K in different dykes of the swarm or even in different parts of the same dyke.

The deposition of mostly Superior-type BIFs in Canada, which were formed in the Late Archean – Early Proterozoic, also shows that the surface temperature at that time was high enough both for TFFI and re-heating processes. This is consistent with the data displaying that at about the same time (ca 2.44 Ga) regional re-heating and remagnetization of the Archean basement took place in the mafic dykes of the Russian Karelia, eastern Fennoscandian Shield (Mertanen *et al.*, 1999). The presences of two blocking temperature peaks in rocks from the late Archean Shelley Lake granite (Dunlop *et al.*, 1982) attest to TFFI at two different temperatures or secondary changes in rock magnetization.

One of the main oxidizing agents during the evolution of early Earth was sulphur, and the formation of giant quantities of pyrite and pyrrhotite during that time is known (Holland, 1984; Rasmussen and Buick, 1999). Thick deposits of pyrite were found in rocks upwards of 2.5 Ga; pyrite cannot be formed with significant exposure to oxygen (Holland, 1984; Rasmussen and Buick, 1999). Pyrite is one of the

essential components of BIFs, and is also held as an indicator of an anoxic environment (Holland, 1984). At the same time, pyrite has a temperature range of its stability and of its formation. Data of Grapes and Challis (1999) and of Marschik and Fontboté (2001) indicate that the temperature of pyrite formation is generally between 601 and 773 K, but could be up to 1015 K (Brostigen and Kjekshus, 1969). The author's investigation shows that the minimum temperature of pyrite formation is in the range of 573 – 733 K (Pilchin, 1985). It is obvious that the temperature of pyrite formation is mostly within the temperature range of TFFI. Since sulphur is not active enough to replace the oxygen in iron oxides, pyrite could be formed by the direct reaction of sulphur with native iron, which may have been produced in significant amounts during TFFI through reaction (5.1). Since both native iron and pure sulphur are very active elements, such reactions as the formation of pyrite and pyrrhotite are very viable. The melting point of sulfur is 388.2 K (Lide, 2004) and its boiling point is 717.6 K (Meyer, 1976; Lide, 2004). This means that within a temperature range of 388.2 – 717.6 K, sulfur would be present in liquid form; and at 717.6 K and higher, it would be present as vapor in the atmosphere. Meyer (1976) shows that at high temperatures the viscosity of liquid sulfur decreases rapidly, and it becomes extremely reactive toward almost every chemical. It is credible that sulfur was present as a liquid in the formation of pyrite. In this case, the surface temperature should have been below or equal to 717.6 K. This would place a constraint on the conditions of pyrite formation to a temperature range of about 573-717.6 K. This temperature interval is within the temperature range of TFFI, and also corresponds to temperatures of high activity of both native iron and pure liquid sulfur, which makes the formation of pyrite or pyrrhotite a very likely outcome.

Another problem of the formation of the Early and Middle Precambrian rocks is that they are felsic in the absolute majority. Felsic rocks are known to contain less amounts of titanium than mafic magmatic rocks, and so titanomagnetites do not play so important a role in their magnetization as in mafic basalts. The felsic composition of Archean magmatic rocks means that the temperature of the magma-ocean was perhaps not high enough for the formation of basalts near Earth's surface. At the same time, rocks of the magma-ocean could have contained a lot of iron, because such neighbours of Earth as the Moon and Mars contain a huge amount of iron in their crust and mantle; not to

mention chondrites (Clark, 1982; Anderson, 1990). This is consistent with the formation of giant quantities of BIFs in Archean cratons containing mostly felsic rocks. Thus, the time span of the formation of BIFs (~ 2 billion years) means that either the cooling of Earth's surface was very slow, or that there were several periods of heating – cooling processes.

Since felsic magmatic rocks contain much less titanium than mafic magmatic rocks, their content of titanomagnetites, if any, would also be lower. Absence of titanomagnetites in felsic rocks of the Early and Middle Precambrian (including the Archean and part of Early Proterozoic) could be an indication of a long, slow cooling during which all titanomagnetites were completely oxidized into magnetite. Another cause of the less significant role of titanomagnetites in the magnetism of felsic rocks could relate to the fact that felsic magmatic rocks were formed at temperatures significantly lower than those of the formation of titanomagnetite solid solution. For example, different authors note that the temperature of crystallization of titanomagnetites is within the range of 1153-1218 K (Lawson *et al.*, 1987), and 1273 K (Honig and Aragón, 1986) to 1573 K (Butler, 1998). These temperatures are much higher than the melting point of most felsic rocks. This could explain why titanomagnetites are absent or do not play a significant role in the magnetic properties of felsic rocks. This coincides with the rare presence of ilmenite in carbonatites (Gaspar and Wyllie, 1983a), and the fact that magnetite is a characteristic mineral of nearly all carbonatites (Gaspar and Wyllie, 1983b).

The formation of hematite in any deposits, for example in BIFs, could take place as a secondary alteration some time between the initial formation of the rocks/deposits and the present time. It was mentioned above that during the formation and the beginning of solidification of the magma-ocean, there was no chance for a liquid water ocean to exist. This means that all the water was in vapour form in the atmosphere. Taking into account that the early atmosphere was anoxic until the Early Proterozoic (main time range of BIFs deposition), it is evident that the formation of hematite on this stage was unlikely. It also means that different processes, including both TFFI through reaction (5.1) and some kind of oxidation of ferrous iron into ferric could have led to the formation of magnetite. Only when conditions changed and both oxygen and water were present, could magnetite have

been partially or completely converted to hematite. However, the formation of hematite cannot relate to an exact period of geologic history, and it would be a prolonged process during which the transformation could be slow or even very slow in terms of geologic time.

Many authors indicate that the rocks of BIFs and/or associated rocks are metamorphosed (Gole and Klein, 1981; Savko, 1994; Gross, 1996a; Miyano and Beukes, 1997; Savko and Poskryakova, 2001; Johnson *et al.*, 2003; Klein, 2005, etc.). Savko (1994), Savko and Poskryakova (2001), and Klein (2005) note that the Late Archean BIFs are in close association with amphibolites. For example, metamorphic conditions for ore bodies of the Zapadno-Kodintsovsky area were defined as  $T=923\pm 30$  K,  $P=500$  MPa, and  $fO_2=10^{-17}$ - $10^{-20}$ . In contrast, metamorphic conditions of rocks associated with Early Proterozoic BIFs of the Kursk Magnetic Anomaly (KMA) were defined as  $T=643$ - $833$  K,  $P=200$ - $300$  MPa, with oxygen fugacity near the magnetite-hematite buffer, and strong Na activity (Savko and Poskryakova, 2001). The mentioned authors also demonstrate that maximum temperatures of the metamorphism of iron-formations of the Mikhailovsky area (KMA) did not exceed 833-873 K. Miyano and Beukes (1997) show that metamorphism at the Penge Iron Formation of the Transvaal Supergroup took place at 693–733 K and  $260\pm 80$  MPa as a result of the intrusion of the Bushveld Complex. This means that if some BIFs were formed during metamorphic processes, the temperature of these processes should be accepted as the temperature of BIFs deposition. At the same time, if metamorphic processes affected BIFs after their formation, the magnetic properties of the rocks of these BIFs should have been changed by the metamorphic temperatures at the time of metamorphism. We believe that it is clear for both scenarios that relatively high temperatures were involved in BIFs deposition, and that the most voluminous Early Proterozoic BIFs were formed in the temperature range of TFFI.

Based on the obvious relationship between some BIFs and metamorphic processes, a research was accomplished on the abundance of the main kinds of metamorphic processes in the Precambrian. Results of this investigation are presented in Figure 6.2.

It is clear from Figure 6.2 that during the Archean, only greenschist, amphibolite, and granulite



metamorphic facies were present, and that during the Early Proterozoic the same kinds of metamorphic facies were abundant. On the other hand, low-temperature and high-pressure metamorphic facies were very rare in the Precambrian. This proves that there were only high and relatively high temperature conditions during the Archean and Early Proterozoic. Results of an analysis of thermodynamic conditions for different kinds of metamorphic facies are displayed in Table 6.5.

Analysis of Figure 6.2 indicates that greenschist metamorphism was the main metamorphism to take place during the Early Archean, and greenschist and granulite rocks were the main metamorphic rocks of the Middle Archean, Late Archean, and Early Proterozoic. Interestingly, the maximum of the formation of greenschist and granulite facies rocks was reached in the Early Proterozoic. In contrast, amphibolites started to play a significant role only from the Late Archean and Early Proterozoic, reaching their maximum in the Middle Proterozoic. This means that water played a limited role in metamorphic processes during the Archean and Early Proterozoic. It should be noted that conditions for the metamorphism of greenschist facies were favourable during Early and Middle Archean, and would still have been widespread in the Late Archean and Early Proterozoic. Data from Table 6.5 show that the average temperature for the

metamorphism of greenschist facies of 681 K, with a standard deviation of 64 K, is within the temperature range of TFFI. That BIFs were formed in greenstone belts, which are known for the presence of metamorphic rocks of greenschist facies, is additional evidence that the surface temperature of and temperatures at shallow depths within the upper crust were within the range of TFFI. Significant distribution of metamorphic rocks of granulite facies in Late Archean and Early Proterozoic rocks supports the presence of high temperature conditions within the crust during these periods.

Estimations of the quantity of iron ore deposited in BIFs show that the sedimentation peak of the Early Proterozoic age is by far the most significant, and includes approximately 90% of all known iron-formations (James, 1983). This makes conditions of the deposition environment in the Late Archean and Early Proterozoic extremely important for understanding the formation of BIFs. Some known processes and features which took place during that period, can be employed for the analysis of those conditions.

Important features and processes for understanding the evolution of Earth in the Late Archean and Early Proterozoic are:

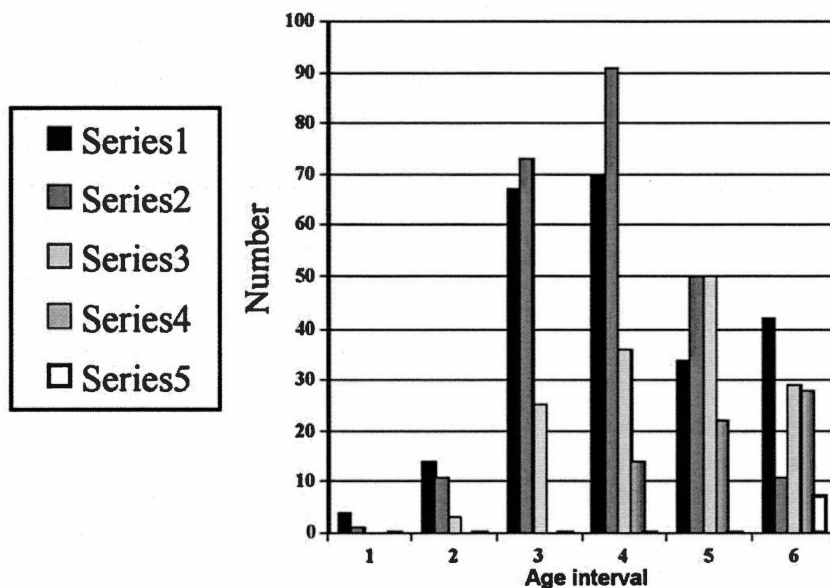


Fig. 6.2. Abundance of main kinds of metamorphism during the Precambrian. Age intervals are corresponding to: 1 - Early Archean, 2 - Middle Archean, 3 - Late Archean, 4 - Early Proterozoic, 5 - Middle Proterozoic, 6 - Late Proterozoic; Facies of metamorphism: Series 1 - Greenschist facies, Series 2 - Granulite facies, Series 3 - Amphibolite facies, Series 4 - Eclogite facies, Series 5 - Blueschist facies.

Table 6.5

Thermodynamic conditions of some metamorphic processes in orogeny accretion zones

| Type of metamorphism | Average T, K | $\sigma_T$ , standard deviation of temperature, K | Average P, GPa | $\sigma_P$ , standard deviation of pressure, Gpa | Average $P/T^*$ , MPa/°C | r, correlation coefficient between T and P |
|----------------------|--------------|---|----------------|--|--------------------------|--|
| Blueschist (n=225)   | 677          | 83  | 1.00           | 0.32   | 2.49                     | 0.64                                       |
| Eclogite (n=469)     | 859          | 120   | 1.91           | 0.67   | 3.22                     | 0.70                                       |
| Amphibolite (n=353)  | 925          | 93  | 0.78           | 0.23   | 1.19                     | 0.58                                       |
| Granulite (n=543)    | 1075         | 89  | 0.82           | 0.27   | 1.02                     | 0.44                                       |
| Greenschist (n=127)  | 681          | 64  | 0.42           | 0.17   | 1.04                     | 0.17                                       |

\* - Average value  $P/T$  was calculated as average of  $n$  ratios  $P/T$

- The maximum reaching temperatures in the mantle corresponding to the widespread formation of komatiites in the Middle and Late Archean, with the peak of komatiites formation around 2.8-2.7 Ga (Arndt *et al.*, 1979; Arndt and Nisbet, 1982; Barley *et al.*, 2000; Svetov and Smolkin, 2003),
- Worldwide magmatic event during the Late Archean (2.75-2.65 Ga) (Rey *et al.*, 2003; Barley *et al.*, 2005),
- Worldwide formation of the largest BIFs (James, 1983; Huston and Logan, 2004),
- A 2.48-2.45 Ga superplume event (Amelin *et al.*, 1995; Heaman, 1997; Barley *et al.*, 1997; Isley and Abbott, 1999; Bekker *et al.*, 2003; Melezhik, 2006),
- Formation of Early Proterozoic dyke swarms (Aspler and Chiarenzelli, 1998; Buchan *et al.*, 1998, Mertanen *et al.*, 1999, Buchan and Ernst, 2004),
- Early Proterozoic glaciations (ca. 2.45-2.22 Ga; Young, 1991; Bekker *et al.*, 2005),
- The great oxidation event (Karhu and Holland, 1996),
- The second superplume event of around 2.25 Ga (Cadman *et al.*, 1993; Davis 1997; Martin *et al.*, 1998; Bekker *et al.*, 2003),
- Early Proterozoic komatiite and picrite magmatism (Arndt *et al.*, 1979; Arndt and Nisbet, 1982; Svetov and Smolkin, 2003),
- A major carbon isotope excursion between ca. 2.22-2.06 Ga (Karhu and Holland, 1996; Bekker *et al.*, 2003),
- Start of plate tectonics in the Early Proterozoic (Hamilton, 1998; Eriksson *et al.*, 2001; Sharkov and Bogatikov, 2001; Deming, 2002; Lenardic *et al.*, 2004, etc.),
- Start of rifting and final breakup of the Kenorland supercontinent at 2.1-2.0 Ga (Aspler and Chiarenzelli, 1998; Bekker *et al.*, 2003).

High-magnesian komatiites, which were formed at the highest temperatures (about 1973 – 2123 K), were developing in most Archean cratons. Since komatiites have the highest melting temperatures among all known magmatic rocks, their formation could be viewed as the indicator of the maximum temperature in the upper mantle. Komatiites appeared in the Middle and Late Archean, and the maximum of their activity was reached at about 2.8-2.7 Ga (Arndt *et al.*, 1979; Arndt and Nisbet, 1982; Barley *et al.*, 2000; Svetov and Smolkin, 2003). Another peak of komatiite and picrite magmatism activity took place in the Early Proterozoic, and it can be regarded as the second temperature maximum in the upper mantle. Analysis of temperatures of high-magnesian magmas formed in the Archean and the Early Proterozoic accomplished by Svetov and Smolkin (2003) for the Fennoscandian Shield points to the decrease of the temperatures of magma formation from the Archean (1973 – 2123 K) to the Early Proterozoic (1846 K). This means that even though both periods of komatiites formation are characterized by a

maximum of temperature, there was a cooling process in the upper mantle during the Archean – Early Proterozoic period. The Late Archean peak of komatiite magmatic activity coincides with a worldwide magmatic event taking place during 2.75-2.65 Ga (Rey *et al.*, 2003; Barley *et al.*, 2005). Thus, we can conclude that the temperature of both the upper mantle and crust during this period was very high. This means that there was at least one temperature minimum between the time of magma-ocean solidification and the temperature maximum related to the peak of komatiite magmatism at about 2.8-2.7 Ga.

The Late Archean and early Paleoproterozoic are characterized by a maximum of both the quantity of BIFs and the quantity of iron ore deposits within BIFs (Gross, 1983; James, 1983; Gross, 1996a, 1996b; Huston and Logan, 2004). Interestingly, the maximum quantity of Algoma-type BIFs was deposited during 2.8-2.7 Ga (Figure 6.3), a period of time that coincides with the beginning of worldwide magmatic activity. This correlates to the abovementioned fact of the formation of Algoma-type BIFs at temperatures higher than those of the formation of Superior-type BIFs. At the same time, the maximum quantity of Superior-type BIFs and the maximum quantity of iron ore were deposited during the period of 2.5-2.4 Ga; and the second maximum quantity of Superior-type BIFs

deposition, along with the second maximum quantity of iron ore deposits, was during the period of 1.9-1.8 Ga. Distribution of both Algoma- and Superior-types of BIFs through time are presented in Figure 6.3. The number of BIFs of both types is displayed for intervals of 100 Ma. Interestingly, there were no Algoma-type BIFs deposited during periods of time between 2.60-2.35 Ga, 2.30-2.20 Ga, and 2.15-2.00 Ga (Huston and Logan, 2004). At the same time, there were no Superior-type BIFs deposited during periods of time between 2.95-2.70 Ga, 2.35-2.15 Ga, and 1.85-1.70 Ga (Huston and Logan, 2004). Some researches point to the decline of BIFs deposition between 2.47 and 2.40 Ga (Barley *et al.*, 2005), and a lack of BIFs deposition during the time period of from 2.4 to around 2.0 B.y. ago (Isley and Abbott, 1999; Canfield, 2004). Data of Huston and Logan (2004) display that there was no deposition of BIFs at about 2.33-2.15 Ga.

There is a growing amount of data showing that there was a superplume event during the very beginning of the Early Proterozoic. The superplume event took place during the period of 2.48-2.45 Ga, and caused the formation of large igneous provinces with mafic volcanic and plutonic rocks (Amelin *et al.*, 1995; Heaman, 1997; Barley *et al.*, 1997; Isley and Abbott, 1999; Bekker *et al.*, 2003; Melezhik, 2006). Barley *et al.*, (2005) believe that this superplume event took place

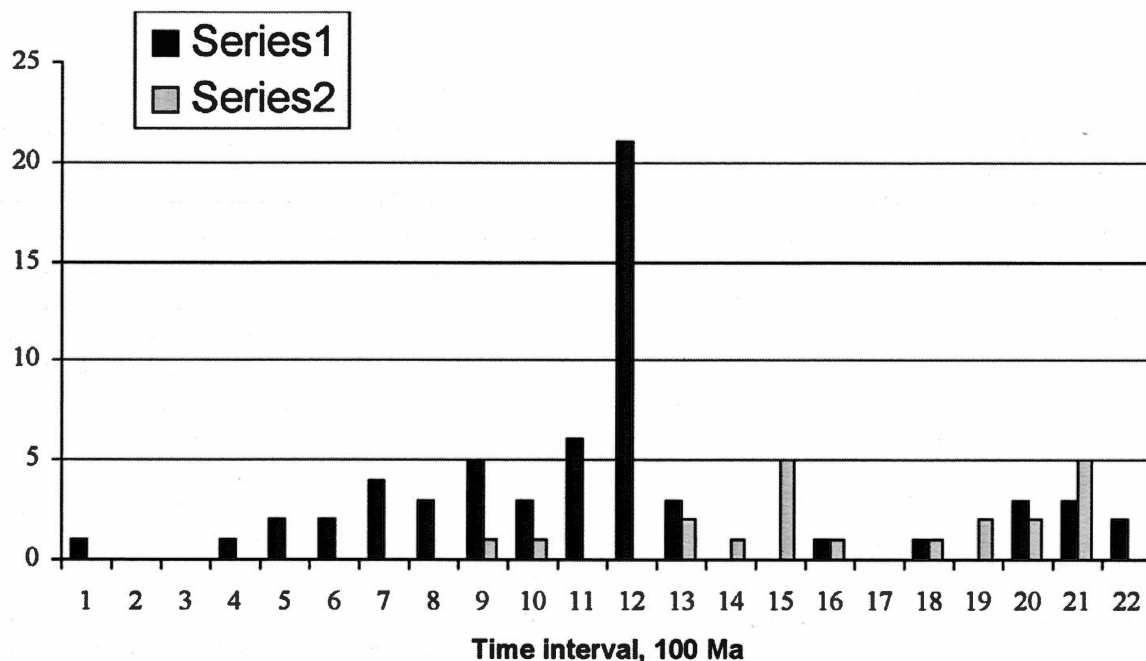


Fig. 6.3. Distribution of BIFs (Algoma-type BIFs – Series 1, and Superior-type BIFs – Series 2) through time. Period of deposition of BIFs from 3.85 Ga to 1.7 Ga is separated to 22 time intervals by 100 Ma each starting from 1 – (3.9 – 3.8 Ga), to 22 – (1.8 – 1.7) Ga.

during ~2.51 to 2.45 Ga; while Mertanen *et al.* (1999) estimated that this event took place around 2.44 Ga at the Baltic Shield. Mertanen *et al.* (1999) showed that at about 2.44 Ga, the Archean basement in the eastern Fennoscandian Shield was re-heated and remagnetized. The fact that remagnetization took place suggests the presence of temperatures in the range of TFFI at that time period in the eastern Fennoscandian Shield, because the remagnetization of rocks usually takes place at temperatures of above 473 K (see Chapter 8). This period of superplume formation coincides with the appearance of the first dyke swarms; there is only a single Archean dyke swarm of ~2.505 Ga reported so far (Buchan and Ernst 2004). Early Proterozoic dyke swarms started their development from 2.47 Ga (Aspler and Chiarenzelli, 1998; Buchan *et al.*, 1998; Mertanen *et al.*, 1999; Buchan and Ernst, 2004), and their development continued with a few discontinuities until 1.88 Ga (Buchan and Ernst, 2004). The worldwide formation of dyke swarms has two clear discontinuities: the first taking place between ~2.37 Ga and ~2.24 Ga, and the second between ~2.17 Ga and 2.10 Ga. Each gap is different for different regions. For example, the formation of the Early Proterozoic dyke swarms of Canada has a clear discontinuity between 2.45 Ga and 2.24 Ga, and a second discontinuity between 2.19 Ga and 2.12 Ga. It is obvious that the first gap in the formation of dyke swarms coincides with the Early Proterozoic glaciation, and the second coincides in time with <sup>13</sup>C excursion during 2.22-2.06 Ga. From a physical point of view, the formation of dyke swarms could take place only in two cases: 1) a fast cooling of the outermost layers of the crust accompanied by a slow cooling of the layers of the middle and lower crust, and possibly the lower part of the upper crust; or 2) a fast heating of the lower and middle crust, with a slow heating of its uppermost layers. The fact of different age ranges of the formation of dyke swarms for different Archean cratons means that there was a different cooling regime and different conditions for these cratons. It is also possible that different cratons had different relative elevation, and cratons with higher elevation would undergo cooling first. This factor is obviously crucial to glaciation, which is another feature that is undeniably related to temperature conditions of the Earth's surface and atmosphere. Three discrete levels of glacial diamictite developed in the Early Paleoproterozoic in the Snowy Pass Supergroup of the Medicine Bow Mountains and Sierra Madre, Wyoming, USA (Bekker *et al.*, 2005) and the Huronian

Supergroup, Ontario, Canada (Hannah *et al.*, 2004; Kopp *et al.*, 2005). Some authors believe that the first global glaciation took place at ~2.4–2.2 Ga (Williams and Schmidt, 1997; Eriksson *et al.*, 2001; Hannah *et al.*, 2004; etc.). Even though there is some evidence of glacial events that took place around 2.9 Ga (Crowell, 1999; Kopp *et al.*, 2005), extensive low-latitude glaciation occurred only near the beginning (2.45–2.22 Ga), and the end (0.73–0.58 Ga) of the Proterozoic eon (Crowell, 1999; Hoffman and Schrag, 2002), with no evidence of large ice sheets at any palaeolatitude for the span of about 1.5 billion years in between these two snowball eras (Hoffman and Schrag, 2002; Pavlov *et al.*, 2003). Signs of the Early Proterozoic glaciation were found in Canada (Williams and Schmidt, 1997; Hoffman and Schrag, 2002; Hannah *et al.*, 2004; Kopp *et al.*, 2005, etc.), South Africa (Hoffman and Schrag, 2002; Kopp *et al.*, 2005), Australia (Lindsay and Brasier, 2002), and the Fennoscandian shield (Mertanen, 2001; Lindsay and Brasier, 2002).

At the same time, some authors believe (Kopp *et al.*, 2005) that the only global glaciation was the Makganyene glaciation of South Africa (2.2-2.3 Ga). A comparison of the time ranges of the Early Proterozoic glaciations shows that they coincide with both discontinuities of the deposition of BIFs, and the formation of the Early Proterozoic dyke swarms. Absence of significant amounts of BIFs during the glaciation periods could mean that the deposition of BIFs could take place only at relatively high temperatures, and that the average temperature was not high enough and periods of high temperature were not long enough for the formation of BIFs. The very fact of glaciations is an unambiguous sign of significant cooling of Earth's surface; reaching, at least in some regions, temperatures below the freezing point of water. However, this does not mean that the entire surface of Earth was below the freezing point of water. On the other hand, the presence of early Proterozoic glaciations point to conditions of cooling of Earth's surface during the first period of the formation of Early Proterozoic dyke swarms. This means that early Paleoproterozoic BIFs containing the absolute maximum quantity of iron ores were deposited in cooling temperature environments. The interchange between periods of the formation of dyke swarms with periods of glaciation shows that it was a regime of a formation of fractures within the uppermost layers of the crust, which were formed by extensional forces generated by cooling and the increase of brittle properties of cooling rocks. At

the same time, deeper regions of the crust still needed to be very hot to provide magma for forming dykes. The more basic composition of dykes compared to their host rocks could be explained by the involvement of water, which reduced the melting temperature of the rock and partially removed alkali elements.

Obvious discrepancies in time between the earliest magmatic events in the Early Proterozoic and the first of three Huronian glaciations show that the first glaciation was not a worldwide glaciation; even though it was a regional one, it could have taken place in a few regions around the world. However, the second glacial period of the Huronian glaciations possibly took place worldwide, or at the least was much more widespread throughout the world. At the same time, the formation of dykes and glaciations at close to— or about the same— time periods during the Early Proterozoic could mean that there was a significant cooling of the surface, and that this cooling was affecting various regions and altitudes differently. Mountain areas could have been covered with snow and ice; but in valley areas, the temperature would have been sufficiently hot enough to support the presence of melt at shallow depths within the crust. In reality, the difference between the highest point on Earth (Mt. Everest – 8848 m high) and the deepest point in the ocean (Mariana trench— 11 022 m deep) is 19 870 m. It is obvious that such a significant difference in elevation would cause a significant difference in the temperatures between these two points. This difference could have been much greater during the evolution of early Earth; and before the formation of the ocean, the temperature difference between the surface temperature and the temperature at the highest mountain peaks could have been a giant one. For example, the Olympus Mons, the largest known volcano in the solar system, has a base of about 600 km across and its peak stands about 26 km above the average Martian surface level (Bennett *et al.*, 2004). It is obvious that the area of the formation of glaciation around the peaks of the highest mountains could have a significant size, but remain local to the peaks, and not take place at lower elevations of the planet. Undoubtedly, such glaciation would not necessarily be worldwide. However, during the subsequent weathering and possible destruction of such a mountain, signs of glaciation could spread and be deposited in different places; not to mention that they would be mixed with deposits of different ages. Interestingly, carbonate strata are known only directly above the middle diamictite of Vagner and Bottle Creek

formations in the Medicine Bow Mountains and Sierra Madre, respectively, and the Espanola Formation in southern Ontario (Bekker *et al.*, 2005).

The great oxidation event, which took place about 2.3 Ga (Karhu and Holland, 1996), means that beginning from that moment the content of free oxygen in the atmosphere started to increase. The appearance of free oxygen in the atmosphere means that there was a presence of both free oxygen and water, and that the formation of ferric iron oxide was possible from then and on. This could explain the formation of red beds and paleosols after the beginning of atmospheric oxidation. The start of the oxidation of the atmosphere could also mean that most oxidation processes involving chemical elements more active than iron were completed, and it was now iron's turn to consume oxygen.

The second superplume event of around 2.25 Ga that formed extensive plateau basalts and dyke swarms (Cadman *et al.*, 1993; Davis, 1997; Martin *et al.*, 1998; Bekker *et al.*, 2003) shows that there was a new period of heating of the upper crust layers and the Earth's surface. During this period, a second stage of rifting also took place (Bekker *et al.*, 2003). This rifting event indicates an extensional regime in the upper crust, which was caused by a faster heating of the middle and lower crust than the upper crust. The formation of dyke swarms starting at ~2.24 Ga supports the presence of such an extensional regime. The formation of magnesium-high magmatic rocks, such as komatiites and picrites close to the end of the Early Proterozoic shows that the heating of the upper mantle and crust started at about 2.25 Ga and continued almost to the end of the Proterozoic, and the maximum temperatures were reached during the formation of those komatiites and picrites.

Karhu and Holland (1996) and Bekker *et al.*, (2003) indicate that the major carbon isotope excursion between ca. 2.22-2.06 Ga is not associated with any known glaciation, and it took place after the Early Proterozoic glaciation event ended.

Many latest publications suggest that plate tectonics did not operate prior to the Early Proterozoic (Hamilton, 1998; Eriksson *et al.*, 2001; Sharkov and Bogatikov, 2001; Lenardic *et al.*, 2004; etc.). This points to conditions of when lithosphere blocks were not separated from one another either because of melt

in the lower crust and upper mantle or because of lack of tectonic processes (for example, rifting) leading to the breakup of young solid lithosphere into blocks. Even though the formation of dyke swarms points to the presence of extensional processes, these processes did not lead to the formation of lithospheric blocks, and the fractures that were formed were simply filled with magma. At the same time, there are some obvious signs of the triggering of rifting in the Early Proterozoic. Some researches point to the start of rifting and final breakup of the Kenorland supercontinent at about 2.1-2.0 Ga (Aspler and Chiarenzelli, 1998; Bekker *et al.*, 2003). This could be a major event leading to the formation of lithospheric blocks. Moreover, this time interval coincides with the time of the formation of dyke swarms after the second discontinuity. This means that the period of time starting from about 2.1 Ga was characterized by a new phase of extensional tectonic developments. This time period is also characterized by the formation of the first ophiolites and the first known obduction processes in the world (Pilchin, 2005).

Fe-Mg silicates of Early Proterozoic BIF rocks of the Kursk Magnetic anomaly (KMA), one of the largest iron ore deposits in the world, are represented by aegirine, riebeckite, and low-Al chlorite (Savko *et al.*, 2003). The decomposition of riebeckite, leading to the formation of aegirine, takes place at a temperature of 783-793 K (Miyano and Beukes, 1997). Savko and Poskryakova (2001) show that this transformation could take place in a temperature range of 673-773 K, and even below 673 K under conditions of strong Na activity in the fluid phase. Paragenesis of aegirine with seladonite, tetraferribiotite, carbonates, and chlorites under conditions of high oxygen fugacity also shows that aegirine was produced at temperatures below 673 K (Savko *et al.*, 2003). This supports the above conclusion that oxygen plays a more important role in TFFI at temperatures below 673 K. At the same time, the absence of hydrothermal iron deposits in the Archean and Early Proterozoic suggest the absence or limited role of hydrothermal activity at that period of time.

All of the above point to the necessity for relatively high temperatures during the deposition of BIFs. It was mentioned above that the maximum quantity of the Algoma-type BIFs was deposited during the Late Archean maximum of magmatic activity. Algoma-type BIFs are usually interbedded with volcanic rocks (Gross, 1996a). Gross (1996a) indicates that the

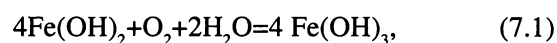
Algoma-type BIFs deposits were formed both near to and distant from extrusive centers along volcanic belts, deep fault systems, and rift zones, and may be present at any stage in a volcanic succession.

Isley *et al.* (1999) believe that the deposition of all BIFs was related to magmatic activity; it is argued that the deposition of the Kuruman and Griquatown Iron Formations is also related to magmatic activity (Johnson *et al.*, 2003). Some other investigators point to the deposition of BIFs during magmatic activity in the Early Proterozoic (Amelin *et al.*, 1995; Barley *et al.*, 1997; Heaman, 1997; Isley and Abbott, 1999; Schneider *et al.*, 2002; Bekker *et al.*, 2003, Krapez *et al.*, 2003; Melezhik, 2006). Ashley *et al.* (1998) also note the high temperature conditions during the deposition of iron formations. At the same time, Ashley *et al.* (1998) argue that the deposition of iron-formations and associated rocks is caused by high-temperature (623 –923 K) oxidizing in saline fluids.

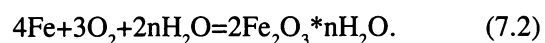
It is evident that in all referenced cases, the temperature was within the range of TFFI. This proves that thermodynamic conditions, and primarily temperature, play a crucial role in TFFI.

## 7. WHY DID NOT EVERYTHING TURN TO RUST?

Thus, TFFI controls the appearance and stability of some iron-containing minerals (Pilchin and Pilchin, 1998; Pilchin and Eppelbaum, 2004). In reality, within the temperature range of TFFI, ferrous iron is unstable and would be transformed into ferric iron. Such a transformation represents the known process of corrosion/rusting of iron. The main reactions representing the rusting of iron are related to the fact that Iron(II) hydroxide is unstable in air:



and the reaction of the rusting of native iron could be presented as:



It is clear from reactions (7.1) and (7.2) that the presence of both oxygen and water is necessary.

Based on this transformation of Iron(II) into Iron(III) and backwards, the special coefficient of FeO

transformation ( $\nu$ ) introduced earlier (Pilchin and Khesin, 1981), is defined as

$$\nu = \text{FeO} / (\text{FeO} + \text{Fe}_2\text{O}_3). \quad (7.3)$$

Here, FeO and Fe<sub>2</sub>O<sub>3</sub> are the contents of Iron(II) and Iron(III) oxides, respectively.

The coefficient  $\nu$  was used for the analysis of the relative Iron(II) content in different rocks and minerals (Pilchin and Eppelbaum, 1997,2004), including rocks of the same genetic origin formed during different geologic periods in various regions and for various types of eclogites and basalts. It was shown earlier (Pilchin and Khesin, 1981; Pilchin and Eppelbaum 1997) that parameter  $\nu$  could be used for the estimation of oxidation conditions during the formation of rocks and minerals. On the other hand, both igneous and metamorphic rocks obviously passed through the temperature range of TFFI during their cooling. This means that it is likely that in both of these kinds of rocks TFFI should take place and ferrous iron oxide should be transformed into magnetite, hematite, or a mixture of both. With the aim to examine this

transformation, the chemical compositions of the main kinds of rocks and minerals were analysed. For the analysis of the relative content of ferrous iron oxide in different kinds of rocks and minerals, as well as for similar rocks from various regions and of various age, a huge amount of data was collected and processed (Tables 7.1 – 7.12). The collected data are compiled into special groups: the values of the relative content of ferrous iron oxide ( $\nu$ ) for some typical rocks generalized from different sources are displayed in Tables 7.1 and 7.2; the value  $\nu$  for granitic and basaltic rocks, as well rocks from the Mid-Atlantic ridge is presented in Tables 7.3 —7.5; Tables 7.6 and 7.7 show the value  $\nu$  for rocks from the rises of the East Pacific Ocean and sedimentary rocks, respectively; Tables 7.8 – 7.10 illustrate the value  $\nu$  for loess and silt, pelitic rocks, and metamorphic rocks, respectively; and in Tables 7.11 and 7.12, information about partially crystallized basaltic rocks, and various rock types before and after their reaction with granitic magma is presented, respectively.

After the complete oxidation of FeO into Fe<sub>3</sub>O<sub>4</sub> (magnetite), the value of  $\nu$  would reach 0.31; and

**Table 7.1**

Relative content of ferrous iron oxide in some rocks (calculated using data of Clark (1982), in wt%)

| Rock                                   | $\nu$     | Fe total, % |
|--|-----------|-------------|
| Continental crust                      |           |             |
| Sedimentary layer                      | 0.48      | 5.79        |
| “Granitic” layer                       | 0.59      | 4.86        |
| “Basaltic” layer                       | 0.63      | 7.64        |
| Oceanic crust                          |           |             |
| Sedimentary layer                      | 0.17      | 5.57        |
| Layer II                               | 0.56      | 7.60        |
| “Basaltic” layer                       | 0.74      | 9.20        |
| Alkalic rocks                          | 0.45-0.62 | 4.42-12.45  |
| Granitic rocks                         | 0.38-0.71 | 1.91-5.27   |
| Intermediate rocks                     | 0.39-0.72 | 3.84-9.70   |
| Gabbroic-basaltic rocks                | 0.73-0.76 | 10.47-11.89 |
| Peridotites                            | 0.80      | 12.35       |
| Rocks from Mid-Atlantic ridge          | 0.65-0.86 | 6.57-12.74  |
| Rocks from rises of East Pacific Ocean | 0.64-0.87 | 9.00-11.79  |
| Ultramafic rocks from orogenic belts   | 0.77-0.98 | 7.59-10.20  |
| Sediments                              | 0.21-0.69 | 1.40-7.00   |
| Metamorphic rocks                      | 0.56-0.69 | 3.60-11.40  |
| Average for igneous rocks              | 0.52      | 6.88        |
| Average for sediments                  | 0.37      | 5.55        |

correspondingly, for the total oxidation of ferrous oxide to ferric oxide, the value of  $\nu$  would be 0. This means that if there is a value for  $\nu$  of less than 0.31, the oxidation conditions would be extremely strong and FeO would be oxidized more than it is necessary for converting all FeO into Fe<sub>3</sub>O<sub>4</sub>. Calculated values of  $\nu$  using data of Dobrzhinetskaya (1985) for gabbroids, metabasalts, and acidic metaeffusives of the Baikal-Vitim greenstone belt (Russia) gave minimum values of 0.13, 0.28 and 0.15; and maximum values of 0.83, 0.99, and 0.89, respectively. These values indicate that even in the same region, oxidation conditions could be

different for different samples and different areas. Some deep-sea sediments are extremely rich in Fe<sub>2</sub>O<sub>3</sub>; for example, the content of ferric iron oxide in red clays and radiolarian ooze could contain 11.83 and 14.99 wt.%, respectively (Clark, 1982).

Calculated values of the parameter  $\nu$  of ferrous iron stability in Tables 7.1 – 7.12—are consistent with similar values presented in our previous publications (Pilchin and Khesin, 1981; Pilchin and Eppelbaum, 1997, 2004). Analysis of the values for parameter  $\nu$  from Tables 7.1 – 7.12 indicates that the values of  $\nu$  are

**Table 7.2**

Relative content of ferrous iron oxide in some typical magmatic rocks

| Rock                         | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | FeO+ Fe <sub>2</sub> O <sub>3</sub> | Calculated using data of |
|------------------------------|--|-------------------------------------|--------------------------|
| Cenozoic Basalt              | 0.68                                       |                                     | Morse, 1994              |
| Island alkali olivine basalt | 0.70                                       |                                     | "-----"                  |
| Olivine basalt               | 0.72                                       | 12.50                               | Turner & Verhoogen, 1960 |
| Alkali olivine basalt        | 0.78                                       | 11.33                               | Hall 1995                |
| Olivine-norite               | 0.86                                       | 8.00                                | "-----"                  |
| Quartz-norite                | 0.94                                       | 9.60                                | "-----"                  |
| Pelitic xenolith             | 0.54                                       | 32.80                               | "-----"                  |
| Basalt                       | 0.66                                       | 11.40                               | "-----"                  |
| Granite                      | 0.59                                       | 2.90                                | "-----"                  |
| Continental crust (average)  | 0.60                                       | 6.50                                | "-----"                  |
| Granodiorite                 | 0.66                                       | 4.10                                | "-----"                  |
| Andesite                     | 0.55                                       | 7.30                                | "-----"                  |
| Sovite                       | 0.33                                       | 9.12                                | "-----"                  |
| Ankeritic carbonatite        | 0.79                                       | 13.20                               | "-----"                  |
| Calcite carbonatite          | 0.30                                       | 3.26                                | Woolley & Kempe, 1989    |
| Dolomite carbonatite         | 0.62                                       | 6.34                                | "-----"                  |
| Ferrocyanatite               | 0.42                                       | 12.72                               | "-----"                  |
| Natrocyanatite               | 0.82                                       | 0.28                                | Keller & Spettel, 1995   |
| Rhyolite                     | 0.43                                       | 2.59                                | Hall, 1995               |
| Trachyte                     | 0.43                                       | 5.28                                | "-----"                  |
| Phonolite                    | 0.42                                       | 4.82                                | "-----"                  |
| Nephelinite                  | 0.53                                       | 11.65                               | "-----"                  |
| Alkali basalt                | 0.77                                       | 12.85                               | "-----"                  |
| Olivine tholeiite            | 0.88                                       | 11.02                               | "-----"                  |
| Tholeiite                    | 0.72                                       | 11.34                               | "-----"                  |
| Muscovite granite            | 0.69                                       | 1.09                                | "-----"                  |
| Biotite-hornblende granite   | 0.73                                       | 3.32                                | "-----"                  |
| Riebeckite granite           | 0.50                                       | 6.02                                | "-----"                  |
| Shale                        | 0.49                                       | 7.00                                | "-----"                  |
| Greywacke                    | 0.58                                       | 5.50                                | "-----"                  |
| All sediments                | 0.38                                       | 5.30                                | "-----"                  |



**Table 7.3**

Relative composition of ferrous iron oxide in granitic rocks (calculated using data of Clark (1982), in wt%)

| Rock (n)                | FeO/(FeO+<br>Fe <sub>2</sub> O <sub>3</sub> ) | Total<br>Fe | TiO <sub>2</sub> | TiO <sub>2</sub> /<br>Fe <sub>2</sub> O <sub>3</sub> |
|-------------------------|---|-------------|------------------|--|
| Alkali granites (48)    | 0.59  | 1.91        | 0.20             | 0.26   |
| Alkali rhyolites (21)   | 0.44  | 2.32        | 0.17             | 0.13   |
| Granites (72)           | 0.66  | 2.53        | 0.37             | 0.43   |
| Rhyolites (22)          | 0.38  | 2.00        | 0.22             | 0.18   |
| Quartz monzonites (121) | 0.65  | 3.49        | 0.56             | 0.46   |
| Quartz latites (58)     | 0.48  | 3.43        | 0.42             | 0.25   |
| Granodiorites (137)     | 0.66  | 3.92        | 0.57             | 0.43   |
| Rhyodacites (115)       | 0.51  | 4.37        | 0.66             | 0.31   |
| Quartz diorites (58)    | 0.71  | 4.78        | 0.62             | 0.46   |
| Dacites (50)            | 0.57  | 5.24        | 0.64             | 0.29   |

**Table 7.4**

Relative content of ferrous iron oxide in basalts

| Rock  | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | Calculated using data of |
|---|--|--------------------------|
| Cenozoic Basalts  | 0.678                                      | Morse, 1994              |
| Island alkali olivine basalts                           | 0.704                                      | "-----"                  |
| Olivine basalts, New Zealand                            | 0.72                                       | Turner & Verhoogen, 1960 |
| Alkali basalt, New Zealand                              | 0.708                                      | "-----"                  |
| Olivine nephelinite, New Zealand                        | 0.636                                      | "-----"                  |
| Basalts   | 0.59                                       | "-----"                  |
| Hawaiian basalts  | 0.798                                      | "-----"                  |
| Picrite, Shiant Isles                                   | 0.956                                      | "-----"                  |
| Picrite basalt, Mauna Loa, Hawaii                       | 0.56                                       | "-----"                  |
| Flood basalts and traps                                 | 0.68                                       | Yaroshevsky, 1997        |
| Alkaline olivine basalts on platforms                   | 0.60                                       | "-----"                  |
| Volcanic associations: midocean ridges                  | 0.84                                       | "-----"                  |
| Volcanic associations: oceanic islands<br>and seamounts | 0.71                                       | "-----"                  |
| Plateau basalts   | 0.73                                       | Birch, 1942              |
| Alkali olivine basalt                                   | 0.78                                       | Hall, 1995               |
| Basalt  | 0.66                                       | "-----"                  |
| Hawaiite  | 0.60                                       | "-----"                  |
| Trachybasalt  | 0.63                                       | "-----"                  |
| Alkali basalt   | 0.77                                       | "-----"                  |
| Olivine tholeiite                                       | 0.88                                       | "-----"                  |
| Tholeiite   | 0.72                                       | "-----"                  |
| Tholeiitic basalts                                      | 0.76                                       | Clark, 1982              |
| Alkali olivine basalts                                  | 0.73                                       | "-----"                  |

**Table 7.5**

Relative content of ferrous iron oxide in rocks from Mid-Atlantic ridge (calculated using data of Clark (1982), in wt%)

| Rock (n)                           | FeO/(FeO + Fe <sub>2</sub> O <sub>3</sub> ) | Total Fe |
|------------------------------------|---|----------|
| Oceanic tholeiite (depth 2910 m)   | 0.74  | 10.49    |
| Oceanic tholeiite (depth 2388 m)   | 0.80  | 7.80     |
| Oceanic tholeiite (depth 3566 m)   | 0.73  | 10.36    |
| High-alumina basalt                | 0.86  | 9.68     |
| Basalt (depth 3700 m)              | 0.79  | 10.43    |
| Basalt (depth 3600 m)              | 0.74  | 8.37     |
| Alkali-olivine basalt (2000-3000m) | 0.65  | 12.74    |
| Laminated gabbro (4000-5000 m)     | 0.65  | 6.57     |

**Table 7.6**

Relative content of ferrous iron oxide in rocks from rises of East Pacific Ocean (calculated using data of Clark (1982), in wt%)

| Rock                        | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | Total Fe |
|-----------------------------|--|----------|
| Glassy basalt (2300m)       | 0.87                                       | 11.79    |
| Basalt, drill core (3746 m) | 0.64                                       | 9.00     |

**Table 7.7**

Relative content of ferrous iron oxide in sedimentary rocks (calculated using data of Clark (1982), in wt%)

| Rock (n)                                   | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | Total Fe |
|--|--|----------|
| Sandstones (253)                           | 0.21                                       | 1.40     |
| Sandstones from platforms (3700)           | 0.37                                       | 4.00     |
| Greywackes (61)                            | 0.69                                       | 5.10     |
| Shales from geosynclines (277)             | 0.57                                       | 6.50     |
| Shales from platforms (6800)               | 0.32                                       | 6.50     |
| Tillites (68)                              | 0.53                                       | 7.00     |
| Limestones (93)                            | 0.57                                       | 2.28     |
| Carbonate rocks from platforms (1500-8300) | 0.40                                       | 1.68     |
| Cherts (10)                                | 0  | 2.3      |

**Table 7.8**

Relative content of ferrous iron oxide in loess and silt (calculated using data of Clark (1982), in wt%)

| Rock (n)                       | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | Total Fe |
|--------------------------------|--|----------|
| Loess near Galena, Ill.        | 0.16                                       | 3.12     |
| Loess Vicksburg, Miss.         | 0.28                                       | 3.28     |
| Loess Kansas City, Mo.         | 0.04                                       | 3.37     |
| Loess Kansu, China             | 0.40                                       | 3.87     |
| Summer silt Leppakosi, Finland | 0.43                                       | 7.60     |
| Siltstone Iron River, Mich.    | 0.88                                       | 12.79    |

**Table 7.9**

Relative content of ferrous iron oxide in pelitic rocks (calculated using data of Clark (1982), in wt%)

| Rock (n)                              | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | Total Fe |
|---------------------------------------|--|----------|
| Clays, shales, and atates (85)        | 0.51                                       | 6.21     |
| Phyllites, schists, and gneisses (70) | 0.70                                       | 6.71     |

**Table 7.10**

Relative content of ferrous iron oxide in some metamorphic rocks (calculated using data Clark (1982), in wt%)

| Rock (n)                    | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | Total Fe |
|-----------------------------|--|----------|
| Phyllites                   | 0.62                                       | 7.80     |
| Mica schists                | 0.69                                       | 6.7      |
| Two-mica gneisses           | 0.64                                       | 5.3      |
| Quartzo-feldspatic gneisses | 0.56                                       | 3.60     |
| Amphibolites                | 0.68                                       | 11.40    |

**Table 7.11**

Comparison of relative content of ferrous iron oxide in some partially crystallized basaltic rocks (calculated using data of Hall (1995), in wt%)

| Rock                  | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | FeO+ Fe <sub>2</sub> O <sub>3</sub> |
|-----------------------|--|-------------------------------------|
| Alkali olivine basalt |  |                                     |
| Rock                  | 0.78                                       | 11.33                               |
| Glass                 | 0.69                                       | 3.98                                |
| Nepheline basanite    |  |                                     |
| Rock                  | 0.84                                       | 12.80                               |
| Glass                 | 0.77                                       | 3.98                                |

**Table 7.12**

Comparison of relative content of ferrous iron oxide using average compositions of various rock types before and after reaction with granitic magma (calculated using data of Hall (1995), in wt%)

| Rock                 | FeO/(FeO+ Fe <sub>2</sub> O <sub>3</sub> ) | FeO+ Fe <sub>2</sub> O <sub>3</sub> |
|----------------------|--|-------------------------------------|
| Argillaceous rocks   |  |                                     |
| Unmodified rock      | 0.61                                       | 6.6                                 |
| Xenoliths in granite | 0.85                                       | 7.4                                 |
| Limestones           |  |                                     |
| Unmodified rock      | 0.33                                       | 0.9                                 |
| Xenoliths in granite | 0.71                                       | 7.6                                 |
| Basic igneous rocks  |  |                                     |
| Unmodified rock      | 0.74                                       | 10.9                                |
| Xenoliths in granite | 0.77                                       | 11.2                                |

the lowest for sedimentary rocks, somewhat higher for felsic rocks, higher for basic rocks, and the highest for ultramafic rocks. Comparison of values  $\nu$  in Tables 7.1 – 7.12 with its value for magnetite ( $\nu = 0.31$ ) demonstrates that this value is below that of magnetite only for some sedimentary rocks (Tables 7.1, 7.7, and 7.8), which were likely formed at temperatures below that of the lower temperature limit of TFFI (~473-523K). This means that the oxidation state and content of ferric iron oxide of these rocks is higher than that of magnetite. Interestingly, the lowest values of  $\nu$  are found for the oceanic sedimentary layer (see Table 7.1). At the same time, the values of  $\nu$  for oceanic magmatic rocks are significantly higher than those of continental magmatic rocks (Tables 7.1 – 7.5), even though oceanic magmatic rocks had obvious contact with such a strong oxidizing agent as water. Table 7.11 displays results of a comparison between the parameter of ferrous iron stability for the rock and glass of two magmatic rocks. The comparison illustrates that in both cases the value of  $\nu$  for rock is higher than it is for glass. Table 7.12 displays results of a comparison of values of the parameter  $\nu$  for unmodified rock, and a similar rock affected by granitic magma. Values of  $\nu$  for rocks affected by granitic magma are much higher than those of the original rocks, even for rocks of sedimentary origin. This obviously points to the transformation of ferric iron into ferrous iron during heating from granitic magma.

In addition to the analysis of the ferrous iron content in different rocks and minerals, the  $\nu$  value was analysed for some non-uniform groups of rocks and spinels (Table 7.13) collected from numerous publications. The data of Table 7.13 demonstrate that for most samples of spinel, the value of  $\nu$  is less than or equal to 0.31.

This means that these spinel samples represent a range of composition from magnetite (for  $\nu = 0.31$ ) to solid solutions containing some amount of magnetite (for  $\nu < 0.31$ ). For different non-uniform groups of Archean and Post-Archean rocks and xenoliths (Table 7.13), it can be clearly seen that only for a very small amount of the samples is the value of  $\nu$  less than or equal to 0.31, and the absolute majority of rocks have this value above 0.60. Low values of  $\nu$  for garnet peridotite xenoliths and rocks of orogenic massifs could be explained by the serpentinization and strong alteration of these rocks. In the case of garnet peridotites, the low value of  $\nu$  is also related to the issue

of numerous researches accepting the iron content of garnet peridotites as only FeO, thereby making it impossible to find real values of  $\nu$  using the data from those researches.

Data from Tables 7.1 –7.13 indicate that in almost all cases, ferrous iron oxide is stable, and the oxidation state of the rocks is in most cases significantly lower than the oxidation state of magnetite. This means that, even though all magmatic and metamorphic rocks passed through the conditions of the temperature range of TFFI, this transformation was only partial. The stability of ferrous iron oxide in almost all rock types supports the fact that TFFI does not usually occur below 473 K. It should be stated that high values of  $\nu$  were found not only for magmatic rocks of a young age, but also for magmatic rocks of the Archean and Proterozoic ages (Pilchin and Eppelbaum, 1997). This data raises a very important question: how is it possible that the iron contained in most rocks did not turn to rust during their direct– or close to direct– contact with the atmosphere, containing vast amounts of oxygen for about the last 2 billion years?

It is known from chemistry that for the corrosion of iron to take place (formation of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}(\text{OH})_3$ ),

the involvement of both oxygen and water is necessary (Akhmetov, 1992; Lide, 2004). Iron would not corrode in water if oxygen were absent, and nor would it corrode in oil in the presence of oxygen (Akhmetov, 1992). This is consistent with the results of various authors, showing that in dry conditions the product of the oxidation of iron and ferrous oxide is magnetite and not hematite (Ikornikova, 1960; Grønvold *et al.*, 1993; Berndt *et al.*, 1996; Shull *et al.*, 1996). The necessity of both oxygen and water for the formation of ferric oxide is also supported by the results of experimental research (Benali *et al.*, 2001) showing that hydroxycarbonate green rust has been synthesized by the oxidation of an aqueous suspensions of  $\text{Fe}(\text{OH})_2$ , by aeration at the air-liquid interface. König *et al.* (1999) reported of clay minerals in deep-sea sediments containing Iron(II), which readily oxidize into Iron(III) upon contact with atmospheric oxygen. At the same time, without such contact, it would still be Iron(II). This fact also supports the necessity of both oxygen and water for Iron(II) oxidation, and suggests the absence of free oxygen at great sea depths of some cases. On the other hand, the natural dehydration of goethite (or laboratory heating to 573–673 K) produces hematite, and is an important process in the formation of red sediments (Butler, 1998). Based on these results, one could assume that a

**Table 7.13**

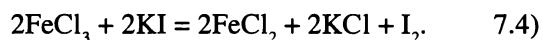
Value of relative content of ferrous iron oxide ( $\nu$ ) in some groups of rocks and spinels

| Rock                        | FeO/(FeO+Fe <sub>2</sub> O <sub>3</sub> ) | Number of samples | Average FeO+Fe <sub>2</sub> O <sub>3</sub> |
|-----------------------------|---|-------------------|--|
| Archean rocks               | 0.60 – 0.97                               | 546               | 5.81                                       |
|                             | 0.50-0.59                                 | 49                |  |
|                             | 0.32-0.49                                 | 57                |  |
|                             | ≤0.31                                     | 47                |  |
| Garnet Peridotite xenoliths | 0.01-0.54                                 | 188               | 7.25                                       |
| Rocks from orogenic massifs | 0.01-0.60                                 | 26                | 8.00                                       |
| Post Archean rocks          | 0.50-0.98                                 | 593               | 6.61                                       |
|                             | 0.32-0.49                                 | 23                |  |
|                             | ≤ 0.31                                    | 7                 |  |
| Spinel                      | 0.35-0.52                                 | 8                 | 8.31                                       |
|                             | 0.0-0.31                                  | 107               |  |
| Xenoliths                   | 0.6-0.99                                  | 428               | 8.93                                       |
|                             | 0.50-0.59                                 | 27                |  |
|                             | 0.32-0.49                                 | 51                |  |
|                             | ≤ 0.31                                    | 22                |  |

very low content of  $\text{Fe}_2\text{O}_3$  (high relative content of ferrous iron,  $v$ ) in oceanic basalts means that there was a presence of water, but not of free oxygen. This also supports the fact that for the formation of mostly  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}(\text{OH})_3$  (rust), there is a necessity for the presence of both free oxygen and water (moisture conditions). At the same time, sediments formed in the ocean sometimes (see Tables 7.1, 7.7, 7.8) have a value of the relative content of ferrous iron ( $v$ ) less than that of magnetite ( $v=0.31$ ), which means that these rocks are richer in  $\text{Fe}_2\text{O}_3$  (ferric iron) than magnetite, and that there were good conditions for the formation of ferric iron at the expense of ferrous iron. This could be explained by the fact that most sedimentary rocks are formed at the low depths of oceans, in which water is rich in free oxygen and the presence of water is also well established. At the same time, the fact that oceanic magmatic rocks have higher values of  $v$  than continental magmatic rocks allows for the assumption that this value is strongly dependent on the cooling rate of magma.

In reality, the cooling rate of an underwater eruption would be much quicker than one taking place on the continent. This is in agreement with earlier reported results (Watkins *et al.*, 1970) showing that for the investigated pillow basalt, cooling rates exceeded oxidation rates. It is also known that pillow basalts of the mid-ocean ridge basalts (MORBs) show a substantial change in textural and mineralogical features as a function of the cooling rate, which is crucial for the characterization of the magnetization of MORBs (Zhou *et al.*, 2000). A higher rate of cooling means that the rock will pass through the temperature range of TFFI more quickly. The longer ferrous iron is exposed to a temperature within the range of the stability of ferric iron and the range of TFFI, the greater the chances that TFFI would take place.

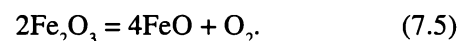
It was mentioned above that the presence of some elements and their oxides could stabilize ferrous iron oxide, preventing its transformation into ferric iron oxide, even within the temperature range of TFFI. Some reactions could conversely change Iron(III) to Iron(II). For example, such a reaction is presented by Akhmetov (1992):



Experiments show (Cairanne *et al.*, 2003) that hematite reduction in the presence of pyrite and CaO

led to the formation of anhydrite and magnetite at 30 MPa and 723 K.

During a heating process, TFFI could run backwards by converting ferric iron oxides to ferrous iron oxides through reaction:



Taking into account that ferric iron is unstable under high temperatures, reaction (7.5) could lead to a significant increase of oxygen fugacity in the lower crust and upper mantle, as well as play a role in the increase of the oxygen level in the atmosphere.

The abovementioned features, processes, and reactions which could stabilize ferrous iron or prevent it from undergoing TFFI, were what prevented temperature factors and oxidizing agents from turning all iron into rust.

Red beds and paleosols are markers of conditions with the presence of both water and oxygen. However, this does not mean that they could not have been altered at a much later time after their deposition; the possibility of which is supported by the “red bed controversy” in paleomagnetism (Butler, 1998; Beck *et al.*, 2003). This relates to the fact that the chemical remanence magnetization (CRM) of deposits is acquired during protracted chemical processes occurring for millions of years after deposition. Analysis of several Triassic and earliest Jurassic sedimentary units from the Colorado Plateau region demonstrates (Beck *et al.*, 2003) that the remanent magnetizations measured in them were acquired over an extended period of time, possibly that of about 35 m.y.; and the units are not precisely coeval with the stratigraphic age of the rock. This means that deposited sediments could turn into red beds millions of years after their deposition. It should also be stated that any heating of such deposits to temperatures above the lower temperature limit of TFFI would significantly speed up the process of the formation of red beds and paleosols.

Today, 21% of the atmosphere is oxygen, and its partial pressure has been growing perpetually from  $10^{-6}$  MPa back in the Early Precambrian, to that of 0.021 MPa at present. At the same time, ferrous iron oxide is still the main iron oxide in the Earth strata (see Tables 7.1-7.13). This means that there is more to the problem

of TFFI than the oxygen content in the atmosphere and presence of water.

## **8. SOME GEOPHYSICAL APPLICATIONS OF FERROUS–FERRIC IRON OXIDES TRANSFORMATION**

Most geophysical applications related to iron and its oxides are based on the magnetic and electric properties of iron-containing rocks and minerals. Even though ferrous iron oxide is paramagnetic and ferric iron oxide is antiferromagnetic, only ferric oxide could be part of ferri- and ferromagnetic minerals, excluding magnetite. This means that TFFI could lead to the formation of a magnetic field, which could be measured using magnetic prospecting methods. The observed data could be used for the determination of normal and anomalous magnetic fields, the position of Earth's magnetic poles, for analysis of magnetic characteristics of rock samples and buried objects and for solving a variety of environmental problems. During the last few decades, rock magnetism has become of greater and greater importance in different fields of science and human life. It is extensively used in physics, traditional magnetic and paleomagnetic methods; as well as for solving such problems as those related to the magnetic properties of rocks, oxidation processes, estimation of temperature conditions, environmental magnetic researches, paleoclimate studies, investigation of rock microstructure, etc. All these methods are based on materials generating a magnetic field or reacting on an existing magnetic field.

It is generally accepted that electric currents flowing in the Earth's molten outer core set up Earth's magnetic field by induction, and continue to support it today (Frenkel, 1947; Bullard and Gellman, 1954, Braginsky, 1964; Merrill and McFadden, 1995). This process generates the normal magnetic field of the Earth; however, an anomalous magnetic field is being generated by the magnetic properties of rocks and minerals composing the Earth crust and sometimes even the upper mantle. This makes magnetic geophysical methods extremely important for investigating the Earth crust structure, searching for magnetic rocks and minerals deposits, estimating the temperature within the crust layers and magmatic complexes. In many cases, analysis of the magnetic properties of rock samples could yield important information regarding processes of rock formation, their cooling and oxidation, position of Earth's magnetic poles at the time

of rocks formation, their subsequent remagnetisation and the paleo-environment during rocks formation.

Since the stability of ferric iron decreases with depth within the Earth crust and upper mantle, it is clear that, depending on the geothermal regime in any given region, and oxidation conditions within the crust and upper mantle, there will be a depth at which TFFI will take place. This means that below that depth, ferric-iron-containing minerals will no longer have their strong magnetic properties. On the other hand, each ferromagnetic has a Curie point ( $T_c$ ), above which it is no longer ferromagnetic. These facts show that there are two possibilities for the losing of magnetic properties by iron-containing rocks and minerals: (a) reaching the Curie point, and (b) TFFI.

The depth at which iron-containing rocks and minerals lose their ferromagnetism can be estimated both by geothermal and magnetic methods (Pilchin and Eppelbaum, 1997; Eppelbaum and Pilchin, 2006). Geothermal methods could be employed for the determination of the depth at which the temperature is either that of the Curie point or in the range of TFFI; and magnetic methods could be used for determining the bottom edges of magnetized bodies (BEMB) in the region under study (Eppelbaum and Pilchin, 2006).

### ***8.1 Iron as the main component of magnetic rocks and minerals in Earth's strata***

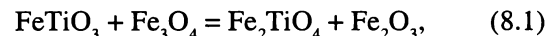
The main magnetic rocks and minerals in the Earth are iron ores and iron-rich rocks and minerals. This is the result of the fact that iron is the most abundant element in the Earth, and iron and its oxides have very particular properties. Iron oxides are presented in rocks and minerals with different magnetic properties in all kinds of magnetic materials (antiferromagnetics, paramagnetics, ferrimagnetics, and ferromagnetics). The most abundant ferrimagnetic and ferromagnetic minerals contain ferric iron oxide ( $\text{Fe}_2\text{O}_3$ ), and most magnetic rocks contain these ferrimagnetic and/or ferromagnetic minerals. The greatest role in rock magnetism, belongs to the magnetic properties of minerals creating natural remanent magnetization (NRM). The magnetic properties of rocks and the stability of their NRM is strongly dependent on the composition, grain-size, and distribution of magnetic minerals within them. Rocks carrying magnetism usually contain a solid solution of magnetic minerals, the magnetic properties of which are sensitive to the

contained magnetic minerals, processes of oxidation, cation ordering, subsolidus exsolution, etc. A change in temperature and/or pressure could break the stability of the rocks and minerals and lead to an alteration of natural magnetization. Numerous researches demonstrate (Dunlop, 1995; Dunlop and Özdemir, 1997; Harrison and Putnis, 1999; Dunlop and Kletetschka, 2001; Dunlop and Özdemir, 2001; Muxworthy and Dunlop, 2002, etc.) that the magnetic properties of minerals are strongly dependent on their grain-size. Usually, magnetic grains are divided into single-domain (SD), pseudo-single-domain (PSD), and multidomain (MD) magnetic grains (Dunlop and Özdemir, 1997; Dunlop and Kletetschka, 2001; Dunlop and Özdemir, 2001; Muxworthy and Dunlop, 2002); and a separate theory was developed for each grain size (Dunlop, 1995; Dunlop and Özdemir, 1997).

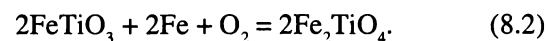
### 8.2 Titanomagnetites – the main carriers of magnetism in basalts

Titanomagnetites are usually accounted as the dominant carriers of magnetism in most basalts (Nagatha, 1961; Pechersky *et al.*, 1975; Zhou *et al.*, 2000; Matzka *et al.*, 2003; Shau *et al.*, 2004; Krása *et al.*, 2005).

Magnetites and titanomagnetites are usually complex solid solutions of different spinel compounds, among which magnetite ( $\text{Fe}_3\text{O}_4$ ) and ulvospinel ( $\text{Fe}_2\text{TiO}_4$ ) are dominant. For instance, a finely exsolved titanomagnetite from Mount Yamaska, Quebec, has a bulk composition of 42%  $\text{Fe}_3\text{O}_4$ , 39%  $\text{Fe}_2\text{TiO}_4$ , 11%  $\text{MgAl}_2\text{O}_4$ , and 8%  $\text{MgFe}_2\text{O}_4$  (Harrison *et al.*, 2002). At higher temperatures, ulvospinel containing ferrous iron oxide is more stable; and at lower temperatures, the magnetite component of the solid solution becomes more stable because of TFFI (Pilchin and Eppelbaum, 1997, 2004), which makes the ferrous-iron-containing ulvospinel less stable. Another Fe-Ti-containing series of solid solutions is represented by titanohematites ( $\text{Fe}_2\text{O}_3 - \text{FeTiO}_3$ ). The composition and content of these solid solutions is also dependent primarily on temperature and oxygen fugacity. At high temperatures, the solution should be ilmenite-rich, since ferric iron oxide is unstable at high temperatures; and at low temperatures, hematite becomes more stable. Andersen and Lindsley (1988) have shown that the chemical equilibrium between solid solutions of titanomagnetite and titanohematite is described by the Fe-Ti exchange reaction



and the stability of ulvospinel is governed by reaction



That reactions (8.1) and (8.2) describe the chemical equilibrium between solid solutions of titanomagnetite and titanohematite is consistent with the results of an investigation of consecutive lava flows of the late Miocene in the Tepic area (Nayarit State, Mexico), showing that the main magnetic mineral in these lavas is Ti-poor titanomagnetite associated with exsolved ilmenite (Goguitchaichvili *et al.*, 2002). Analysis of the Leg 30 samples from a single thick sill, shows them to contain abundant coarse titanomagnetites with fully developed ilmenite exsolution lamellae (Dunlop *et al.*, 1982). Gaspar and Wyllie (1983a) point to the coexistence of magnetite and ilmenite (with low MgO and MnO content) with equilibrium temperatures of 843-868 K in carbonatites of the Jacupiranga Complex, Brazil. Gürsoy *et al.* (2003) reported that ferromagnets in basaltic and andesitic volcanics in Anatolia, central Turkey, are typically titanomagnetites with low Curie points of ~523 K, which usually undergo sub-solidus exsolution to produce ilmenite lamellae hosted by Ti-poor magnetite. This is also supported by the fact that most magmatic rocks contain magnetite and ilmenite as accessory minerals.

It is also obvious that at a high temperature in a magma chamber within the upper mantle, ferric iron oxide would be unstable, and the main component of solid solutions of titanomagnetite would be ulvospinel. Magnetite would be formed primarily during the cooling process at the time of magma uplift, its solidification, and final cooling. The oxidation of  $\text{Fe}_2\text{TiO}_4$  into magnetite during cooling generates solid solutions enriched in magnetite with a decrease of the cooling rate, because it would then be under conditions favourable for TFFI for a longer period of time, obviously with low oxygen fugacity within the rising magma. Since both titanomagnetites and titanohematites are solid solutions involving either ferrous or ferric iron oxides, respectively, TFFI could possibly play an important role in their stability and transformations. TFFI involving ulvospinel would increase the content of ferric iron oxide in the solid solution. This process would also increase the  $T_C$  of titanomagnetites or generate a new component with a

higher  $T_C$ . This means that at a slow cooling rate of basalts, there are more chances for a magnetite-rich component to be formed.

Lawson *et al.* (1987) show that the Fe-Ti oxides in the pumice blocks from Mt. Shasta, California was crystallized at temperatures between 1143 and 1218 K. This means that felsic magmas cannot be rich in titanomagnetites, since most of them have melting points of below 1143 K. It also indicates that titanomagnetites cannot play any significant role in magnetic field of the Archean and Early Proterozoic cratons, which are primarily composed of felsic magmatic rocks.

### **8.3 Transformation of ferrous iron to ferric iron and secondary changes in rock magnetism**

Let us discuss and analyse some other facts, features, and processes, which also denote the presence of TFFI.

Magnetization is obviously related to the magnetic properties of rock-forming minerals; and the presence of ferromagnetic and ferrimagnetic minerals, their concentration, and their dispersion within the rock. A large number of magnetic and paleomagnetic studies illustrate that, during both heating and cooling cycles, significant changes of magnetic properties take place. These changes could involve the formation of new magnetic substances, change of Curie point, increase or decrease of magnetization, and some another parameters. A large number of researches show changes in rock magnetization during heating at temperatures in range of 473–773 K (Yakubovskaya *et al.*, 1980; Nazarova and Gonikberg, 1984; Acton *et al.*, 2000; Hill, 2000; Otofujii *et al.*, 2000; Kechra *et al.*, 2003; Matzka *et al.*, 2003; Shau *et al.*, 2004; Zhu, 2004, etc.).

In many cases, studied samples exhibit bimodal blocking-temperature spectra. Such bimodal blocking-temperature spectra with blocking temperatures in the range of 473 – 853 K were reported for rocks from different regions (Dunlop *et al.*, 1982; Acton *et al.*, 2000; Vlag *et al.*, 2000; Sumita *et al.*, 2001; Calvo *et al.*, 2002; Orlicky and Funaki, 2002; Shau *et al.*, 2004, etc.). Some research results demonstrate change in both the value of  $T_C$  and the quantity of magnetic minerals within the rock during experiments of heating – cooling cycles at temperatures in the range of 623 – 853 K (Watkins *et al.*, 1970; Vlag *et al.*, 2000; Shau *et al.*,

2004, etc.). Some authors point at the presence of a temperature range, rather than at an exact value of blocking temperature (e.g., Dunlop and Özdemir, 2001). Many researchers believe that a special role in rock magnetism belongs to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and/or titanomaghemite (Dunlop and Özdemir, 1997; de Boer and Dekkers, 2001; Matzka *et al.*, 2003; Shau *et al.*, 2004). However, even though maghemite has very strong magnetic properties, it is metastable and would be easily converted into antiferromagnetic hematite. The temperature range of the stability of maghemite is usually within 473 - 623 K (Yakubovskaya *et al.*, 1980; de Boer and Dekkers, 1996; Dunlop and Özdemir, 1997; Alva-Valdivia *et al.*, 2001; Redl *et al.*, 2004; Zhu *et al.*, 2004; Gendler *et al.*, 2005, etc.).

The great variance in values of  $T_C$  and blocking temperatures could be related to the processes of TFFI and remagnetization. Processes of heating, cooling, re-heating, and further cooling could take place in different regions and during different processes (repeating of intrusions or extrusions, repeating of metamorphic processes, etc.). Such processes could change both the magnetic phase and its content in the rocks of a region. It always should be taken into account that even though magnetite has a  $T_C$  of about 848-853 K, it does not mean that any rock containing magnetite was formed above its  $T_C$  and gained its magnetism at its  $T_C$  during the process of cooling. Taking into account reaction (5.1), it is obvious that magnetite could be formed by TFFI at any temperature within the temperature range of TFFI (between 843 K and 473 K), and the newly formed magnetite would still have the same properties and  $T_C$  as magnetite formed under different temperature conditions. Clearly, magnetic minerals cannot get remanent magnetization prior to the formation of the magnetic phase. It is also evident that a magnetic phase formed above its  $T_C$  cannot gain any magnetization until the temperature is reduced to below its  $T_C$ . Titanomagnetite, formed at high temperature, would also not gain its magnetism until it cools below its  $T_C$ . Fast rates of cooling could prevent rocks from significant TFFI. This means that the quantity of the formed magnetite would depend on the rate of cooling, which would be different for rocks formed under different conditions.

The uniqueness of TFFI is that it could take place during both cooling and heating processes. It would start when the temperature within the cooling rock decreases below that of the upper boundary of the



temperature range of TFFI, and would continue until the rock temperature drops below that of the lower boundary of the temperature range of TFFI. At the same time, TFFI would also take place during the heating of a rock as soon as its temperature rises above that of the lower boundary of the temperature range of TFFI. TFFI would start just above 473 K and cause changes to the magnetic properties of the rock. This is consistent with the well-known facts of the presence of broad temperature tails above and below the blocking temperature within which changes in the composition of a magnetic phase and its magnetic characteristics take place (Dunlop and Özdemir, 2001). This signifies that either the magnetic phase of a rock was formed within a temperature interval around the blocking temperature; or that the presence of a blocking temperature does not control TFFI, which is also supported by the “red bed controversy” feature discussed in Chapter 7.

**8.4 What is wrong with these planets? A lot of iron, but no magnetic field**

Even though iron is the primary component of the main types of ferromagnetics and ferrimagnetics, and its content in terrestrial planets is enormous, Earth is the only terrestrial world with the presence of a strong magnetic field. The Moon also has no magnetic field (Bennett, 2004). The values of the magnetic fields of terrestrial planets (after Van Allen and Bagenal, 1999) are presented in Table 8.1.

This fact is in agreement with a theory that states that the magnetic field of planets depends on the presence of an electrically-conducting fluid in its interior region (such as the molten outer core of the Earth), significant convection, and rapid rotation of the planet.

**Table 8.1**

Magnetic field of terrestrial planets

| Planet  | Magnetic field at equator (microTesla) |
|---------|--|
| Mercury | 0.3                                    |
| Venus   | <0.003                                 |
| Earth   | 30.5                                   |
| Mars    | <0.03                                  |

All terrestrial planets contain giant quantities of iron, mostly within their iron core (see Tables 2.5 and 2.6). However, only Earth has a magnetic field of significant value. This means that the iron core has nothing to do with the formation of a normal magnetic field. At the same time, Mars does not have a molten core. Venus has a partially molten core and its molten outer core is much thicker than that of Earth, but the rotation speed of Venus is too slow (Bennett, 2004), and its surface temperature is too high for the presence of any significant amounts of magnetic rocks in its crust. Mercury has a measurable magnetic field (about 1% of Earth’s magnetic field) despite its small size, an absence of or very low content of iron compounds in its crust and mantle, and a very slow speed of rotation. These facts support the idea that both an outer liquid core and a significant speed of rotation of the planet are important for the formation of a magnetic field.

**8.5 Curie point and depth of Curie point. Bottom edge of magnetic object**

One of the key parameters of rock magnetism is the Curie point ( $T_c$ ) of its composing minerals. The Curie point is different for different ferro- and ferri-magnetic minerals, and it characterizes the temperature value at which a rock or mineral loses its magnetic properties and becomes paramagnetic. Curie points of some magnetic minerals and alloys are presented in Table 8.2.

Among the wide range of minerals in all rock types of the Earth’s crust and upper mantle, the most strongly magnetic mineral is magnetite, having a  $T_c$  of ~848-853 K. Another magnetic phase widely spread mostly in mafic rocks is represented by solid solutions of titanomagnetite. These usually have a  $T_c$  between 373 K and 823 K, depending on the content of ulvospinel in the solid solution (Nagata, 1961; Pechersky *et al.*, 1975; Nishitani and Kono, 1983). Values of  $T_c$ , along with geothermal data, could be used for determining a Curie point depth (CPD), which characterizes the bottom edges of magnetized bodies (BEMB) in different regions (Pilchin and Eppelbaum, 1997; Eppelbaum and Pilchin, 2006). The determination of the CPD is one of the most important problems in the examination of regional magnetic anomalies, because along with the determination of the BEMB it helps to define the thickness of the magnetoactive layer. It is necessary to underline that in most cases, values of the CPD (determined by geothermal data) and values of

**Table 8.2**

Curie points of some magnetic materials

| Magnetic matter   | Curie (or Néel) point, K | Reference                |
|---|--------------------------|--------------------------|
| Magnetite Fe <sub>3</sub> O <sub>4</sub>                | 853                      | Dunlop and Özdemir, 1997 |
| Maghemite γFe <sub>2</sub> O <sub>3</sub>               | 863-948                  | "-----"                  |
| TM60 Fe <sub>2.4</sub> Ti <sub>0.6</sub> O <sub>4</sub> | 423                      | "-----"                  |
| Hematite αFe <sub>2</sub> O <sub>3</sub>                | 948 (Néel)               | O'Reilly 1984            |
| Goethite αFeOOH   | 343 – 398 (Néel)         | "-----"                  |
| Cobalt  | 1404                     | Hunt <i>et al.</i> 1995  |
| Magnesioferrite Mg Fe <sub>2</sub> O <sub>4</sub>       | 713                      | "-----"                  |
| Cobalt ferrite CoFe <sub>2</sub> O <sub>4</sub>         | 793                      | "-----"                  |
| Trevorite NiFe <sub>2</sub> O <sub>4</sub>              | 858                      | "-----"                  |
| Nickel Ni   | 631                      | "-----"                  |
| Ilmenite FeTiO <sub>3</sub>                             | ~40 (antiferromagnetic)  | "-----"                  |
| Ulvospinel Fe <sub>2</sub> TiO <sub>4</sub>             | ~120 (antiferromagnetic) | "-----"                  |
| Jacobsite MnFe <sub>2</sub> O <sub>4</sub>              | 573                      | "-----"                  |
| Troilite FeS  | 578 (antiferromagnetic)  | "-----"                  |
| Goethite, α-FeOOH                                       | ~393 (antiferromagnetic) | "-----"                  |
| Lepidocrocite, γ-FeOOH                                  | 177 (antiferromagnetic)  | "-----"                  |

**Table 8.3**

Depths of the CPD, isotherms of 473 and 673 K, and BEMB in the Kura Depression, Azerbaijan (after Pilchin & Khesin, 1981)

| Area        | Depth of 473 K isotherm, km | Depth of 673 K isotherm, km | CPD, km | BEMB, km |
|-------------|-----------------------------|-----------------------------|---------|----------|
| Ismaily     | 5.5-6.5                     | 14-16                       | 25-30   | 14       |
| Shamkhor    | 5.0-6.0                     | 12-13                       | 18-22   | 20       |
| Sarkyar     | 5.5                         | 13-14                       | 22-24   | 18       |
| Borsunly    | 5.5-6.5                     | 14-15                       | 24-28   | 16       |
| Lyaky       | 5.5-6.5                     | 15-17                       | 30-32   | 22       |
| Karajaly    | 5.5-6.5                     | 15-17                       | 30-32   | 14       |
| Sor-Sor     | 6.0-7.9                     | 16-17                       | 30-34   | 13       |
| Ragimly     | 6.0-7.0                     | 16-17                       | 32-34   | 12       |
| Imishly     | 7.5                         | 20-22                       | 44-46   | 11       |
| Comushly    | 7.5                         | 19-21                       | 42-44   | 14       |
| Saatly      | 7.5                         | 18-19                       | 40-42   | 9        |
| Levonarch   | 5.5-6.6                     | 14-15                       | 24-26   | 16       |
| Bashkarvand | 5.5-6.5                     | 15-16                       | 26-28   | 10       |
| Gindarch    | 5.5-6.5                     | 15-16                       | 25-30   | 15       |
| Beilagan    | 6.5-7.0                     | 15-16                       | 25-30   | 26       |
| Pervomai    | 6.5-7.5                     | 19-20                       | 42-44   | 7        |

the BEMB (determined by magnetic data) do not coincide (Pilchin and Eppelbaum, 1997; Eppelbaum and Pilchin, 2006). These values coincide only in regions of deep faulting occurrence.

Pilchin and Khesin (1981) and Eppelbaum and Pilchin (2006) showed that position of the BEMB in

most cases corresponds to depths within the temperature range of TFFI (Tables 8.3 and 8.4).

**8.6 Is Earth's core in a ferromagnetic state?**

Another important feature related to iron and its compounds is the shifting of the Curie point under

Table 8. 4

CPD, depth of isotherms of 473 and 673 K, and BEMB depth for some areas of Israel (after Pilchin and Eppelbaum, 1997)

| Area                                | Depth of 473 K isotherm, km | Depth of 673 K isotherm, km | CPD, km | BEMB, km |
|-------------------------------------|-----------------------------|-----------------------------|---------|----------|
| Ramat HaGolan                       | 13                          | 31                          | 44      | 23-28    |
| Atlit, Carmel                       | 12                          | 30                          | 46      | 22-25    |
| well Belvoir 1 (Galilee)            | 10.5                        | 25.5                        | 44      | 23-27    |
| Rosh Pina, Hazon                    | 10                          | 24.5                        | 46      | 22-26    |
| Between the wells                   | 11.5                        | 28                          | 38      | 25-28    |
| Pleshet1 & Engeddi                  |                             |                             |         |          |
| Boker1 (central Negev)              | 11.5                        | 29                          | 38      | 31-35    |
| South-western coast of the Dead Sea | 10.5                        | 25.5                        | 39      | --       |
| Northern Arava Valley               | 11.5                        | 30                          | 39      | 29-34    |
| Hot Asdod 1 (Ashdod)                | 10.5                        | 26                          | 39      | 23-27    |
| Ashkelon                            | 11                          | 28                          | 38      | 25-29    |
| Be'er-Sheva                         | 13                          | 30                          | 38      | 29-33    |

applied pressure (Slater, 1940; Bozorth, 1951; Patrick, 1954; Schult, 1970; Leger *et al.*, 1972; Morán *et al.*, 2003; Matsushima *et al.*, 2006, etc.). This caused a controversy in the interpretation of the variation of the Curie point with pressure at the end of the first half of the 20<sup>th</sup> century (Bozorth, 1951). This controversy was related to issues of Earth's magnetism. It has been argued that in the interior of the Earth, where the temperature is above the Curie point of a matter, the high pressure may increase the Curie point of the matter and make it magnetic at considerably higher temperatures, and thereby contribute to Earth's magnetism. Some theoretical estimations of a possible shift of the Curie point value (for example, Leipunsky (1938)) were used to support the idea that iron and iron-nickel alloys could be magnetic in the Earth's core at extremely high temperatures. The effect of pressure on the Curie point of some ferro- and ferri-magnetic materials and alloys, as well as of minerals, is presented in Tables 8.5 and 8.6, respectively.

For theoretical estimations of the Curie point shift with pressure, the method of the Clapeyron equation and the quantum exchange interaction curve of Bethe were used (Bozorth, 1951). This curve is referenced in some later publications as the Bethe-Slater curve (Jiles, 1991). The quantum exchange interaction curve of Bethe (Figure 10-13 (Bozorth, 1951)) is actually a plot of the Curie point (in K) as dependent on the ratio  $D/d$ ,

where  $D$  is the lattice spacing and  $d$  is the diameter of the  $3d$  electron shell, responsible for ferromagnetism. The curve has its maximum near cobalt, at about 1400-1500 K. Cobalt is located on this curve close to the maximum and a little bit to the right of it. Manganese and iron are located to the left of the maximum, and nickel and gadolinium are located to the right of it. According to the theory, the Curie points of substances to the right (e.g. nickel) will increase with pressure and pass through the maximum before decreasing. Both the increase and decrease of the Curie point with the increase of pressure for different metals, alloys and minerals (see Tables 8.5 and 8.6) supports this theory. The Bethe curve also correctly separates the ferromagnetic  $3d$ -elements such as iron, cobalt, and nickel from the antiferromagnetic  $3d$ -elements such as chromium and manganese (Jiles, 1991). The important fact is that the actual value of the Curie point of any matter cannot increase to values greater than the maximum defined by the Bethe curve. This means that even at very high pressures, the Curie point of any known substance would not be substantially greater than that of cobalt at atmospheric pressure. This would indicate that ferromagnetic materials could not be present inside the Earth's core (Bozorth, 1951). This theoretical result coincides with experimental data (see Table 8.6) showing that for the content of Ni in FeNi-alloys containing less than 64% of nickel, the shift value of the Curie point is negative, as is the value for pure

**Table 8.5**

Effect of pressure on the Curie point of some ferromagnetic materials and alloys

| Magnetic material                 | Curie Point, K | $dT_c/dP$ , K/100MPa | Reference                       |
|-----------------------------------|----------------|----------------------|---------------------------------|
| Iron                              |                |                      |                                 |
| theoretical                       | 1043           | 1.6, and 1.8         | Morán <i>et al.</i> , 2003      |
| experimental                      | 1043           | 0                    | “-----”                         |
| Iron (theoretical)                | 1043           | -5 to -10            | Bozorth, 1951                   |
| Nickel (theoretical)              | 630            | 0.05                 | Slater, 1940                    |
| Nickel                            | 631            | 0.4                  | Major <i>et al.</i> , 1971      |
| Iron                              | 1043           | -0.05                | Shiga, 1981                     |
| Iron                              | 1043           | 0 (below 1.75 GPa)   | Leger <i>et al.</i> , 1972      |
| Cobalt                            | 1398           | 0 (below 6.0 GPa)    | “-----”                         |
| Nickel                            | 627            | 0.36 (below 6.0 GPa) | “-----”                         |
| Nickel                            | 627            | 0.17 (at 8.0 GPa)    | “-----”                         |
| Ni <sub>30</sub> Fe <sub>70</sub> |                | -4.9                 | “-----”                         |
| Ni <sub>36</sub> Fe <sub>64</sub> |                | -3.5                 | “-----”                         |
| Ni <sub>53</sub> Fe <sub>47</sub> |                | -1.66                | “-----”                         |
| Ni <sub>64</sub> Fe <sub>36</sub> |                | -0.40                | “-----”                         |
| Ni <sub>75</sub> Fe <sub>25</sub> |                | 0.60                 | “-----”                         |
| Ni <sub>93</sub> Fe <sub>07</sub> |                | 0.52                 | “-----”                         |
| Iron (theoretical)                |                | -0.1                 | “-----”                         |
| Nickel (theoretical)              |                | 0.2                  | Patrick, 1954                   |
| Nickel (theoretical)              | 630            | 0.4                  | Leipunsky, 1933                 |
| Nickel (theoretical)              |                | 0.006                | Slater, 1940                    |
| FeNi (30.2 at. % Ni)              | 630            | -5.3                 | Matsushima <i>et al.</i> , 2006 |
| FeNi Invar                        | irradiated     | -3.4 – -4.4          | Wei <i>et al.</i> , 2002        |
| Gadolinium                        | non-irradiated | -1.60                | Robinson <i>et al.</i> , 1964   |

**Table 8.6**

Effect of Pressure on the Curie point of some minerals

| Magnetic material            | Curie point, K | $dT_c/dP$ , K/100MPa | Reference                         |
|------------------------------|----------------|----------------------|-----------------------------------|
| Magnetite                    | 851            | 1.85-1.90            | Schult, 1970                      |
| Magnetite (synthetic)        | 851            | 1.85                 | “-----”                           |
| Magnetite (polycrystalline)  | 851            | 0.47-2.00            | Govindarajan <i>et al.</i> , 1982 |
| Magnetite (single crystals)  | 851            | 1.7-2.2              | “-----”                           |
| Titanomagnetites ( $x=0.2$ ) |                | ~1.65                | Schult, 1970                      |
| Titanomagnetites ( $x=0.4$ ) |                | ~1.45                | “-----”                           |
| Titanomagnetites ( $x=0.6$ ) |                | ~1.35                | “-----”                           |
| Titanomagnetites ( $x=0.8$ ) |                | ~0.80                | “-----”                           |

iron. In reality, the content of Ni in the Earth’s iron core is much smaller than 64%, which means that the Curie point of FeNi-alloy representing Earth’s core will be reduced by pressure, and the iron core will not be ferromagnetic.

## 9. CONCLUSIONS

Analysis of iron abundances in terrestrial planets and meteorites, as well as different features and processes involving iron and its compounds, lead to following conclusions:

Iron is the most abundant element in the Earth, and during Earth accretion and evolution it preserved for Earth a significant part of Earth's total oxygen content.

Ferrous and ferric iron oxides, and the transformation between them played a crucial role during the formation and evolution of Earth, other terrestrial planets, and meteorites. The transformation takes place in the temperature range of 473–843 K. Numerous facts point to the widespread of this transformation in all terrestrial planets, including in the formation of their iron cores.

The transformation of ferrous to ferric iron (TFFI) does not require the presence of oxidizing agents, and could take place in a vacuum. The presence of oxygen could play a significant role at temperatures below 673 K. TFFI could take place during both cooling and heating processes.

Analysis of oxidation processes, changes in magnetic properties of rocks and minerals, and conditions of stability of iron-containing rocks and minerals, shows that the absolute majority of these features and processes took place in the temperature range of 473–843 K, that of TFFI.

TFFI played a significant role in the formation of banded iron formations (BIFs), red beds, and paleosols.

The deposition of BIFs is evidence of a high surface temperature of Earth at the time of their formation. Analysis of the relative content of ferrous iron oxide ( $v = \text{FeO} / \Sigma\text{Fe}$ ) in different rocks and minerals indicates that in most cases its content is higher than of that in magnetite, and that only for some sedimentary rocks (mostly of oceanic origin) is its value less than that of magnetite. Values of  $v$  for oceanic magmatic rocks are higher than corresponding values of this parameter for continental magmatic rocks, which emphasizes the role of the rate of cooling on the stability of ferrous iron oxide.

The first magnetic minerals could have formed only after the cooling of Earth's surface to the temperature of the upper bound of the temperature range of TFFI (~843 K).

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