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LECTURE TEXT

Intriguing minerals: lorandite, $TlAsS_2$, a geochemical detector of solar neutrinos

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Abstract
This lecture text demonstrates how the mineral lorandite is used as a detector of solar neutrinos. Because the age of the lorandite deposit in Allchar, North Macedonia, is known, this opened the possibility to determine the solar neutrino flux over the last 4.3 million years.

Keywords Lorandite · Thallium · Lead · Mineral · Neutrino

Lorandite

Lorandite (or lorándite), $TlAsS_2$, is well known as the most common thallium-containing mineral [1, 2]. It was first discovered in the Allchar mine, Macedonia, in 1894 [3–5], and the first chemical analysis was performed by Loczka [6]. Smaller quantities were later found in other localities worldwide: the Dzhizhikrut Sb–Hg mine in Tajikistan, the Beshtau uranium deposit in Russia, the Lanmuchang Hg–Tl deposit in China, the Zarshuran gold mine in Iran, the Lengenbach Quarry in Switzerland, and three locations in the USA (New Rambler Cu–Ni mine in Wyoming, Jerritt Canyon mines in Nevada, and Mercur gold mine in Utah) [2]. Nevertheless, Allchar remains the richest lorandite-bearing locality in the world.

The monoclinic tabular aggregates of lorandite are typically dispersed throughout the realgar (As_4S_4) and orpiment (As_2S_3) mineral hosts. Well-developed crystals are very rare; however, 32 unique crystal forms have been observed [4, 7, 8]. Lorandite is easily distinguished from realgar by its darker red color, semimetallic luster and perfect cleavage along the (001), (201) and (110) planes. Some crystals are coated with a brownish yellow crust. Lorandite crystals of 1 cm are typical for this site, although exceptional single crystals up to 5 cm have also been found. Lorandite is named in honor of the Hungarian physicist Loránd Eötvös (1848–1919) (Fig. 1).

The Allchar locality has been known since the twelfth or thirteenth century, and according to other estimations, even longer. The chemical composition of lorandite from Allchar was confirmed by Jannasch [9] soon after the first analysis conducted by Loczka [6]. Allchar's lorandite is a pure mineral, containing only traces of K, Cr, Fe, Cu, Pb and Zn [10–16]. The ore-grade in the richest zone contains about 18,000 m^3 of the ore, with an average thallium content of 0.35%. Lorandite is the most heavily exploited sulfosalt mineral from Allchar [17–19] because of its ability to act as a geochemical detector of the solar proton–proton (pp) neutrino flux [20, 21]. Neutrinos are produced in vast numbers by the Sun as a result of ongoing fusion processes taking place in the Sun's interior. It is known that the Sun generates most of its energy via the pp chain, which is responsible for 98.4% of the solar output [22]. In the first reaction of the pp chain, a proton decays into a neutron in the immediate vicinity of another proton. The two particles form the hydrogen isotope deuterium, along with a positron and an electron neutrino (Eq. 1):

$$p + p \rightarrow {}^{2}\mathrm{H} + e^{+} + \nu_{e}. \qquad (1)$$

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Fig. 1 Lorandite from Allchar

Solar neutrino detection

Interest in the Allchar ore locality has increased considerably since 1976, when the American physicist Melvin Freedman (1930–1997) realized that the mineral lorandite could be used as a geochemical dosimeter for the solar neutrino flux. The idea is simple: the Allchar ore locality is the largest lorandite deposit in the world, and its age is known to be 4.31(2) Ma [23]. Since ^{205}Tl interacts with neutrinos according to

$$^{205}\text{Tl} + \nu_e(E_\nu \geq 52\ \text{keV}) \rightarrow {}^{205}\text{Pb} + e^-, \tag{2}$$

the average neutrino flux Φ_ν from the Sun can be calculated using the equation:

$$\Phi_\nu \sigma_\nu = C\frac{N_{^{205}\text{Pb, exp}} - N_{^{205}\text{Pb, B}}}{m\left(1 - \mathrm{e}^{\lambda t}\right)}. \tag{3}$$

$C = 3.79 \times 10^{-19}$ mol a^{-1}, σ_ν: cross section of solar pp-neutrino capture by ^{205}Tl, $N_{^{205}\text{Pb, exp}}$: number of experimentally determined ^{205}Pb atoms per mass m, $N_{^{205}\text{Pb, B}}$: number of ^{205}Pb atoms per mass m formed by background reaction, λ: decay constant of ^{205}Pb ($\lambda = 4.01(16) \times 10^{-8}$ a^{-1}), $t = 4.31(2)$ Ma [2, 24, 25]. In age determinations [26, 27] using the formation and decay of radioisotopes, the activation flux is known and the activation time is calculated, whereas in this case the age is known and the flux is calculated.

Neutrinos were first introduced to physics as hypothetical particles by the Austrian-born theoretical physicist Wolfgang Ernst Pauli (1900–1958) [28]. At that time, Pauli had to cope with the fact that electrons, emitted in ordinary beta decays, exhibited a continuous spectrum, suggesting a three-body rather than a two-body decay. The third particle, which had been postulated and initially named "neutron" by Pauli, was given its current name by the Italian-born American physicist Enrico Fermi (1901–1954) [29], who called it "neutrino", meaning "little neutron" in Italian. The existence of the neutrino (more correctly electron antineutrino $\bar{\nu}_e$) had been seen earlier in recoil experiments [30]. In 1956, the American physicists Clyde Lorrain Cowan Jr. (1919–1974) and Frederick Reines (1918–1998), in collaboration with other scientists [31, 32], discovered the neutrino according to the reaction

$$p + \bar{\nu}_e \rightarrow n + e^+. \tag{4}$$

In recognition of this discovery, Frederick Reines was awarded the 1995 Nobel Prize in Physics, which he shared with the American chemical engineer and physicist Martin Lewis Perl (1927–2014), awarded for his discovery of the tau lepton.

The Sun is a powerful source of neutrinos, which are the product of nuclear fusion reactions taking place in its core (Eq. 1), the total flux of which is $\Phi_\nu = 6.5 \times 10^{10}\ \nu\ \text{cm}^{-2}\ \text{s}^{-1}$ [33]. The basis of solar neutrino detection is the fact that the dominant component in the solar neutrino spectrum consists of so-called pp-neutrinos, whose flux can be determined by means of radiochemical and geochemical detectors [34].

Neutrinos are neutral (uncharged) particles with a mass very close to zero. They possess incredible penetration ability, and travel at nearly the speed of light, from the Sun's to the Earth's surface in around 8 min. Therefore, practically all neutrinos that strike the Earth penetrate to its opposite side. However, an exceptionally small number interact with condensed matter on Earth. In order to count the neutrinos and then to confirm the standard solar model (SSM) proposed by Bahcall [22], which predicts that most of the flux comes from the pp-neutrinos with energies below 0.4 MeV, the American chemist and physicist Raymond ("Ray") Davis Jr. (1914–2006) in 1960 [35, 36] placed 100,000 gallons (= 379 cubic meters) of tetrachloroethylene, C_2Cl_4, at a depth of about 1500 m in a gold mine in the US state of South Dakota. The depth is crucial because it is necessary to eliminate the cosmic radiation effect, which could be registered by the detector, causing inaccurate experimental results. The precise measurements (^{37}Ar produced in the reaction between neutrino particles and ^{37}Cl) lasted about 20 years. Davis confirmed the functionality of the detector, but the number of neutrinos registered amounted to only one-third of the theoretical prediction. This result, which became known as "the solar neutrino problem", confounded physicists for years. Two alternatives were considered: modifying the model or checking the experiments. As a consequence of the unexpected and possibly inaccurate results, various alternative solar neutrino detectors using gallium, lithium, manganese and other elements were considered for future research.

To that end, in 1975, the Argonne National Laboratory in Chicago, Illinois sent a letter to the Yugoslavian government, requesting information regarding the condition of the Allchar deposit, which was known to have the richest concentration of thallium minerals in the world. After receiving an answer from the Yugoslavian government, Professor Melvin Freedman from Argonne National Laboratory visited the Fe–Ni mining company at Kavadarci and Allchar. Freedman et al. [24] proposed thallium as a detector of neutrino activity by measuring the reaction with neutrinos, which transform thallium into lead.

According to Freedman et al. [24], solar neutrino detection was possible based on these rare interactions. The authors proposed that one of the thallium isotopes (^{205}Tl) in the mineral lorandite, which during the interaction with neutrinos transforms into the lead isotope ^{205}Pb (cf. Eq. 2), could be used as neutrino detector. Their idea was to analyze thallium-containing lorandite from Allchar and examine the quantity of transformed ^{205}Tl into ^{205}Pb. This quantity of ^{205}Pb is a basis for calculating the number of neutrinos which over the millennia have passed through lorandite, enabling the calculation of the Sun's flux that could help in determining the Sun's age according to SSM [37]. Freedman et al. [24] considered that by analyzing old thallium minerals, the quantity of lead determined should be equivalent to the number of neutrinos which have passed through the mineral over a period of about five million years, enabling the estimation of total solar activity. The father of the model, the American astrophysicist John Norris Bahcall (1934–2005) [22, 38], at first expressed skepticism regarding Freedman's hypothesis. His reservations about the geochemical detectors, among others, were related to the erosion that occurred at the site over millions of years, which would make it impossible to measure the role of cosmic radiation and the participation of the background radioactivity. However, Freedman's hypothesis was accepted in 1983 by the German scientists (led by Professors H. Morinaga and E. Nolte from the Technical University of Munich), and the locality of Allchar, with its relatively high quantities of lorandite, was chosen for conducting the investigations of solar neutrino detection.

The driving force behind the LOREX project (LORandite EXperiment) of geochemical detection of solar neutrinos has been Miodrag Pavićević, professor of physical chemistry at the Faculty of Mining and Geology, University of Belgrade. Since 1985, the project has been financed by federal government funds. Scientists from several institutions in Macedonia have also participated in the project. New excavations at Allchar's locality were started at a depth of around 30 m. By careful separation of about 10 tons of ore, 1 kg of lorandite was obtained at a steel factory in Skopje [39, 40].

The project was financed by various funds until 2000. The follow-up financing of the German-Yugoslavian project, however, was not approved by the European Union. Miodrag Pavićević is now an honorary professor at the University of Salzburg; the project was financed by the Austrian Government from 2008 to 2010 and was further extended from 2012 to 2015, coordinated by professors Pavićević and Amthauer [40]. The main purpose was to evaluate the erosion around the mine during the period of over four million years of existence of lorandite, and to calculate the input of both cosmic radiation and natural radioactivity during that period. In the meantime, all projects based on the use of geochemical detectors for counting neutrinos were interrupted. In order to promote the project, two international conferences and five international workshops were organized.

The problem of solar neutrinos has since been solved by a series of experiments performed at several places around the world. The most important of these lasted around 20 years and were performed at the Institute for Cosmic Ray Research at the Kamioka Observatory in Japan [41]. Similar experiments were performed at the Sudbury Neutrino Observatory located at the mines in Sudbury, Canada, at a depth of around 2000 m [42]. All of these long-range, expensive experiments have shown that Davis' measurements were sufficiently correct. These fundamental investigations are still in progress, with the final aim of constructing more sensible detectors for solar neutrinos.

From theories for detecting neutrinos to trapping sufficient numbers of this mysterious, almost massless particle over a period of almost 50 years, the heads of both the Homestake experiment and the Super-Kamiokande Neutrino Detection Experiment, Raymond Davis Jr. and Japanese physicist Masatoshi Koshiba, were awarded the Nobel Prize in Physics in 2002, *"for pioneering contributions to astrophysics, in particular for the detection of cosmic neutrinos"*. Only one-third of John Bahcall's calculated rate at which the detector should capture neutrinos was found. This significant discrepancy was eventually explained by neutrino oscillations, a concept once proposed by the Italian nuclear physicist Bruno Pontecorvo (1913–1993) [43].

Allchar is a remarkably interesting and rare mineralogical ore deposit—exploited during certain periods in the past for its ore, but "exploited" at the end of the previous century for fundamental investigations in physics and chemistry [2]. Its importance as a source of ore reserves is well illustrated by the fact that in 2009, the Parliament of the Republic of Macedonia declared the Allchar locality a natural monument by a special law [44]. This legislation designated the Allchar locality as a protected zone where scientific investigations could be undertaken only with special permission from the Ministry of Environment and Physical Planning, although ecotourism was mentioned as a unique type of permitted economic activity. However, in 2012, at the proposal of the Ministry of Environment and Physical Planning, the Parliament of the Republic of Macedonia rescinded the declaration of the Allchar locality as a natural monument [45]. According to a new law, geological explorations to ascertain the presence of economically important quantities of gold, thallium and antimony are permitted, as well as the continuation of the project activities. The real cause for the change in Allchar's status, however, is economic in nature. It is believed that the amount of gold at the Allchar locality ranges between 0.5 and 3 g/t (in total around 20 tons) [46], with an estimated value of about €750 million. For this reason, in 2013, a concession was given for geological exploration of the Allchar locality.

Nevertheless, the activities on the project of solar neutrino detection continue with the support of the Austrian Science Fund. From the research carried out thus far, it can be concluded that a large number of problems regarding the use of lorandite for neutrino detection have been solved. The following has been established:

- Ore bodies with antimony, arsenic and thallium at the Crven Dol (As-Tl) and Central Part (Sb–As-Tl) locations may provide sufficient quantities of ore for separation of "pure" lorandite crystals in quantities of up to several kilograms from at least three different depths [47].
- The content of trace elements, including Pb, U and Th, in lorandite and the co-genetic minerals is very low; thus lorandite has an almost stoichiometric composition [10, 13, 39, 48, 49].
- The geological age of the thallium-richest area ranges from 4.22 ± 0.07 Ma [50] to 4.31 ± 0.02 Ma [23], determined by radiometric methods (K/Ar and ^{39}Ar/^{40}Ar) on various samples from the Allchar locality.
- The maximum erosion rate at the Allchar locality was estimated by one radioactive measurement ranging from ~20 to ~90 m/Ma, depending on the location [40, 51].

Ongoing investigations include reopening underground mines in the Crven Dol and Central Part locations to extract sufficient quantities of lorandite and the co-genetic minerals realgar, orpiment and pyrite. The remaining major challenge will then be determining the neutrino capture probability based on the measured quantity of transformed ^{205}Tl into ^{205}Pb.

The results obtained from geological, mineralogical and geochemical investigations of the Allchar ore deposit, supplemented with investigations scheduled in the near future, promise successful completion of the project of solar neutrino detection using lorandite from Allchar.

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