



Vanadium: Global (bio)geochemistry



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ABSTRACT

Redox-sensitive transition group elements are involved in almost all fundamental geochemical processes. Of these elements, vanadium (V) contributes a particularly powerful tool to decipher the Earth's history and its link to extraterrestrial bodies. A comprehensive view of V includes the formation and interaction between the Earth's interior layers, the evolution of the Earth's surface to a habitable zone, biogeochemical cycling, and anthropogenic impacts on the environment. Tracing the geochemical behavior of V through the Earth's compartments reveals critical connections between almost all disciplines of Earth sciences. Vanadium has a history of application as a redox tracer to address the early accretion history of the Earth, to identify connections between the mantle and crust by subduction and melting, and to interpret past surface environments. The geochemical cycling of V from the deep Earth to the surface occurs through magmatism, weathering and diagenesis, reflecting variations of fO_2 and V species in different Earth compartments. Minerals form a link between deep Earth reservoirs of vanadium and surface environments, and the study of V in minerals has increased the understanding of V cycling. Finally, the exploitation of V has been increasing since the Industrial Revolution, and significant amounts of V have been released as a consequence into natural systems. Environmental concerns are promoting new areas of research to focus on V cycling between water, air, soil and sediment compartments. An increased understanding of V in all compartments, and knowledge of the processes that connect the compartments, is vital to tracing the fate of this intriguing element in natural systems.

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1. Introduction

Vanadium is increasingly applied to studies of almost all fundamental geochemistry disciplines. Research on V geochemistry has, however, lagged behind that for other transition metals. This is the first comprehensive review that addresses the geochemical behavior of V under dramatically different conditions, from the terrestrial Earth to other rocky planets, from magmatic to environmental studies, and from partitioning at high temperature to speciation in hydrous systems. Such a holistic approach is vital to link chemical reservoirs to the evolution of the bulk Earth. Vanadium is widely distributed in igneous and sedimentary rocks and minerals as a mildly incompatible, refractory, lithophilic element. The average crustal abundance of V is similar to that of Zn and Ni (Reimann and Caritat, 1998) although it is more dispersed in the crust than either element; concentrated mineral deposits are consequently rare. Much of the historical interest in V has derived from the occurrence of the common redox states in Earth surface environments (+3, +4, +5) as a consequence of V's geochemical evolution. The chemical speciation and the solubility of V species are strong functions of pH and Eh conditions (Taylor and Van Staden, 1994), making it a key redox indicator. More recently, interest in V partitioning during high temperature – high pressure magma differentiation processes has increased, and new possibilities to exploit V stable isotope chemistry are being explored (Nielsen et al., 2011; Nielsen et al., 2014; Prytulak et al., 2011; Prytulak et al., 2013). Studies on the partitioning of V among the possible reservoirs in the Earth's crust have provided critical insights into the evolution of these reservoirs (Fig. 1).

The lithophilic nature of V explains its predominance in Earth surface environments, where it plays a role in a wide range of biological processes. The function of V in biology likely evolved with the chemical differentiation of the Earth's surface environments. This leads to the intriguing possibility that V played a major role in biological electron transfer early in Earth's history (Rehder, 2008a; Rehder, 2008b).

The complex redox chemistry of V and its particular application to renewable energy technologies will likely add to the demand for this element in the future. The demand for V used in construction materials, by far the greatest consumer of mined V, can be expected to further increase the volume of this element that is cycled through terrestrial, aquatic and atmospheric systems.

In the following, we explore the chemical behavior of V in the Earth's major compartments, including magma, rocks, sediments and organisms as well as in extraterrestrial matter.

2. Vanadium geochemistry in terrestrial earth and planetary systems

2.1. Vanadium distribution in the Earth and in extraterrestrial materials

Knowing the V composition of the major geochemical reservoirs is critical for understanding the geochemical behavior of V in terrestrial magmatism, and for applying V to constrain fundamental processes of the Earth. Such processes include, but are not limited to, core segregation, mantle and atmospheric evolution, and the development of ore deposits.

2.1.1. Meteorite, bulk earth, and moon

The starting point for V on Earth is accretion and core formation. A comparison of the V content between CI chondrites and the Earth provides important constraints on both processes. CI chondrites are considered to represent the primitive undifferentiated materials in the solar system and are likely the most important building blocks from which the Earth was formed (McDonough and Sun, 1995; Palme and O'Neill, 2003; Sun and McDonough, 1989). The average V contents of CI chondrites estimated in a few studies are quite consistent, ranging from 55 to 56.5 mg kg⁻¹ (Anders and Grevesse, 1989; McDonough and Sun, 1995; Palme, 1988; Wasson and Kallemeyn, 1988). These values are lower than the average V contents of the silicate earth (82 mg kg⁻¹) estimated in McDonough and Sun (1995) because V is more depleted in Ca-Al-rich inclusions than are Al and rare earth elements. The bulk V in the CI chondrite is consequently diluted.

The bulk Earth has a V content of 95 mg kg⁻¹, lower than that in the metallic core (120 mg kg⁻¹) (McDonough and Sun, 1995). The ratio of the V content between silicate Earth (or primitive mantle) and CI chondrite normalized to Mg content is 0.62 (McDonough and Sun, 1995), showing a terrestrial depletion. Numerous studies have demonstrated that V depletion is best explained by the preferential partitioning of V into the metallic core at high pressure and low fO₂ during the “deep magma ocean” process (Gessmann and Rubie, 1998; McDonough and Sun, 1995; Palme and O'Neill, 2003; Ringwood et al., 1991; Wänke and Dreibus, 1986). Simple mass-balance calculations show that the core could contain half of the total V budget of the bulk earth (McDonough, 2003). The Moon mantle is depleted in V, as well as in Cr and Mn, similar to the Earth's mantle (Ringwood, 1966; Ringwood et al., 1991). This implies that the Moon was most likely derived from the mantle of the Earth or from an impactor larger than Mars that experienced V depletion due to core forming processes (Drake et al., 1989; Gessmann and Rubie, 2000; Ringwood et al., 1991).

2.1.2. Mantle and crust

Post-accretion processes have led to distinct signatures of V in the mantle and crust. Vanadium contents in peridotites range from a few mg kg⁻¹ to around 100 mg kg⁻¹, substantially lower than the concentration in mid-ocean ridge basalts (MORB), ocean island basalts (OIB), and island arc basalts (IAB) (Fig. 2). This indicates that V is mildly incompatible during mantle partial melting. Clinopyroxene, garnet, and spinel are the main hosts for V in mantle peridotite (Johnson et al., 1990). Because the valence of V is sensitive to fO₂, peridotites from different tectonic settings show variable V contents and correlations with other major trace elements, providing an important tool to constrain fO₂ of the mantle through the Earth's history (Canil, 2002; Canil, 2004). A summary of 6590 basalt samples from spreading centers shows large variations, from less than 100 mg kg⁻¹ to 800 mg kg⁻¹, and gives an average V composition of ~275 mg kg⁻¹ (data from <http://www.petdb.org/>). Similar ranges are also observed in OIB and IAB (see (Mallmann and O'Neill, 2009) for a recent summary) and reflect the effect of source composition, melting degree, and melting style.

Trace element compositions for continental crust can be estimated via weighted averages of a large number of representative rock units

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