

CORRESPONDENCE

How old is silicate oxygen isotope geochemistry? Who were the pioneers?

SIR.—Recent review papers on oxygen isotope variations and their geological applications by Epstein & Taylor (1967), and by Garlick (1969) have come to be regarded as the most comprehensive and authoritative, in contemporary geochemical circles. To a petrologist, new to the field and keen on applying O^{18}/O^{16} techniques to research problems, these two articles appear to convey the impression that the importance of silicate oxygen isotope geochemistry came to be recognized just a few years ago. The purpose of this note is to dispel this possible impression and to show that the importance of applying oxygen isotope techniques to problems posed by terrestrial and extra-terrestrial silicate rocks was recognized nearly 40 years ago soon after Giauque & Johnstone (1929a, 1929b, 1929c, 1929d) discovered O^{18} and O^{17} .

The well-known Russian geochemist Vernadsky appears to be the first one to suggest, as early as 1934, that the isotopic composition of oxygen in deep-seated metamorphic rocks and minerals will be different from that observed in the surficial shells of the earth (Vernadsky, 1934). This was followed by the important research of Manian, Urey & Bleakney (1934) who measured the isotopic composition of oxygen in a granite from Stonington, Maine, and in the stony meteorites Mocs, Knyahinya, and Homestead. Bleakney & Hipple (1935) analysed over 100 samples from various sources, including meteorites, for possible oxygen isotope variations. Two years later, Anderson, *et al.* (1937) investigated the structural hydroxyl water of muscovites from Nellore (Madras, India) and Tanganyika (East Africa). In the early 1940s, Vernadsky, Vinogradov & Teis (1941) studied the oxygen isotopic constitution of hydroxyl water in metamorphic rocks and minerals from the Precambrian of Russia.

Nearly a quarter-century ago, the first serious attempt to develop a suitable method for extracting all the oxygen contained in a variety of terrestrial silicate rocks (granite, basalt, trap rock, dolerite) for isotopic measurements was made by Vinogradov & Dontsova (1947). Soon thereafter, Tokuda & Kashida (1949) investigated the isotopic constitution of oxygen in numerous rock-forming silicate minerals from Japan and China (microcline, augite, chlorite, pyrophyllite, kaolinite, talc, allanite, beryl, idocrase, tourmaline and topaz). During 1949–50, Keith, Davis, Tuve & Doak conducted some experiments to determine the oxygen isotope ratios in samples of quartz of contrasted geological origin, and suggested that O^{18}/O^{16} ratios of quartz, taken in conjunction with other data, might provide a useful clue to geological temperatures (Adams, 1946–50). The same year, Baertschi (1950a) made the interesting suggestion that ‘one of the most important applications of the accurate oxygen isotope ratio determinations in silicate rocks would be the possibility of distinguishing between real igneous rocks and meta-sedimentary rocks’. The problem confronting most of these pioneers, particularly the Russian workers, was whether or not a fractionation of oxygen isotopes had occurred during the primordial formation of the earth’s crust.

Although two excellent objective reviews by Ingerson (1953) and Rankama (1954) fully recognize the importance and significance of the pioneering early work in Russia, U.S.A., Europe and Japan, the Epstein–Taylor and Garlick review papers have not drawn attention to either of these two very important contributions; this is rather surprising. Volborth (1968), however, does draw attention to Rankama’s (1954) summary of the early work, and paradoxically, the only reference to Ingerson’s (1953) contribution is by the Russian geochemist Dontsova (1970) in a paper that appears to be the most objective and concise review of the subject to come out in recent years.

A critical and objective review of the literature pertaining to silicate oxygen isotope geochemistry from the early 1930s up to the present time leads to the following significant conclusions:

(1) Contrary to contemporary impressions in non-Soviet geochemical circles, the Russian geochemists Vinogradov and Dontsova should be regarded as the first ones who were seriously concerned with the problems of: (a) extracting oxygen from a variety of

terrestrial silicate rocks for isotopic measurements so as to obtain 100% oxygen yields, and (b) determining the isotopic composition of oxygen in rock types like granite, basalt, trap rock, and dolerite. Thus, nearly a quarter-century ago, Vinogradov & Dontsova (1947) laid the solid foundations for modern silicate oxygen isotope geochemistry. Dontsova continues to be a very active worker in this field and has contributed several papers of petrological importance and significance through all these years (Dontsova, 1948, 1950, 1954, 1955, 1956, 1959, 1966, 1967a, 1967b, 1968, 1970; Dontsova & Milovskiy, 1967; Dontsova & Naumov, 1967; Dontsova & Gerasimovskiy, 1969; Nesterenko & Dontsova, 1967; Milovskiy & Dontsova, 1968; Vinogradov, Dontsova & Chupakhin, 1958, 1960). Also, Vernadsky appears to be the first one to recognize, way back in 1934, the importance of oxygen isotope variations in rocks and minerals.

(2) As early as 1949, Keith, Davis, Tuve and Doak recognized the petrological and geothermometric significance of O^{18}/O^{16} ratios of quartz (Adams, 1949–50).

(3) Baertschi of the University of Basel, Switzerland, working at the Institute of Nuclear Studies, University of Chicago, U.S.A., was the first one to undertake, at the suggestion of Harold Urey, a systematic oxygen isotope study of igneous, sedimentary and metamorphic rocks, to suggest that oxygen isotopes should prove useful in distinguishing between real igneous rocks and igneous-looking metasedimentary rocks, and also to indicate that magmatic water is enriched in O^{18} relative to sea water (for a summary see Baertschi, 1950a, 1950b).

(4) The progress made in recent years in applying oxygen isotope techniques to problems of igneous, sedimentary, and metamorphic rocks would not have been possible but for the fundamental contributions of Vernadskiy (1934); Manian, Urey & Bleakney (1934); Nier (1940, 1947); Vinogradov & Dontsova (1947); Tokuda & Kashida (1949); Keith, Davis, Tuve and Doak (*in* Adams, 1949–50); Baertschi (1950a, 1950b); Baertschi & Silverman (1951); Baertschi & Schwander (1952); Silverman (1951); and Schwander (1953).

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